Development of Emission Profiles for CaRFG w/o MTBE

Summary

This paper recommends adjustments to the ARB emission profiles for CaRFG blended with MTBE to create profiles for CaRFG blended with ethanol and CaRFG blended without any oxygenate. Each adjustment is based in part on comparing an emission profile for an MTBE-blended CaRFG and, from the same emission study, a profile for an ethanol-blended or oxygen-free fuel that was similar in hydrocarbon composition*. Two studies provide the data for adjusting the base profiles to represent emissions from CaRFG blended with ethanol: (1) the recent ARB testing of an MTBE-blended CaRFG and a fuel with high RVP and ten percent ethanol and (2) a test program sponsored by ARB in 1995, "Effects on Exhaust and Evaporative Emissions of Phase 1 and Phase 2 Gasolines", by Automotive Testing Laboratories. One study provides the data for adjusting the current profiles to represent emissions from oxygen-free CaRFG: "Auto/Oil" Technical Bulletin 17.

In addition, properties of ethanol-blended and oxygen-free CaRFGs predicted in a recent linear-program modeling study sponsored by the California Energy Commission have been input into the ARB's Predictive Model for exhaust emissions of benzene and butadiene and into newly created models for aldehyde emissions and evaporative benzene emissions. These techniques--which are uniquely available for four toxic species--provide additional information on adjusting the contents of those species in the profiles for MTBE-blended CaRFG.

In general, within each emission study, the profiles for the MTBE-blended test fuel are similar to those for the ethanol-blended or oxygen-free test fuel. In most cases, the only significant differences are the interchange (or removal of) the oxygenate and, for exhaust profiles, the interchange of the major partial combustion products of the oxygenates (e.g., more formaldehyde and isobutylene for MTBE and more acetaldehyde for ethanol). The profiles from the MTBE-blended test fuels are usually similar (in some cases, identical) to the current ARB profiles. Therefore, the differences between profiles within the test studies can be applied with confidence to adjust the current profiles.

There is one major exception to the general similarity of profiles within a study: within A/O #17, the stabilized exhaust (FTP bag 2) profiles for MTBE-blended and oxygen-free CaRFGs differ considerably, and they differ strongly from the ARB's current stabilized exhaust profile (#876). Thus, it is not clear how best to create the stabilized exhaust profile for oxygen-free CaRFG to contrast with profile #876.

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* The ethanol-blended test fuels were made with the same hydrocarbon bases as were the MTBE-blended fuels. However, to meet the RVP limit, commercial CaRFGs with ethanol will usually be made with modified hydrocarbon bases; probably, pentane contents will decline and alkylate contents will increase. (Aromatics and olefins will be constrained by the Predictive Model.) Such changes will not involve highly reactive species; so, data from splash-blended test fuels rather than commercial fuels should be adequate here with regard to reactivity.

The recommendations for the various profiles are repeated below from the main report, in a "cookbook" format. They include recommendations for creating fuel-composition profiles for ethanol-blended and oxygen-free CaRFGs by adjusting an existing profile for MTBE-blended CaRFG. The adjustments are based on comparing the predicted in the recent linear-programming study for the CEC.

The three studies cited above provide data from only catalyst-equipped vehicles. Therefore, the adjustments recommended below for the emission profiles for catalyst vehicles must be applied to the existing emission profiles for non-catalyst vehicles as well.

Finally, there are recommendations for adjusting the MVEI for CO.

Ethanol-Blended CaRFG

Extended Diurnal Emissions: Remove MTBE from the ARB profile for MTBE-blended CaRFG. For ethanol-blended CaRFG with 2 percent oxygen, adjust all species in proportion so that their sum is 89 percent and add 11 (mass) percent ethanol to complete the profile. For ethanol-blended CaRFG with 3.5 percent oxygen, adjust all species in proportion so that their sum is 81 percent and add 19 percent ethanol.

Hot-Soak Emissions: Remove MTBE from the ARB profile for MTBE-blended CaRFG. For ethanol-blended CaRFG with 2 percent oxygen, adjust all species in proportion so that their sum is 82 percent and add 18 percent ethanol. For ethanol-blended CaRFG with 3.5 percent oxygen, adjust all species in proportion so that their sum is 69 percent and add 31 percent ethanol. Multiply benzene (in each profile) by 1.06. Again, adjust all species so that they sum to 100% in each profile.

Starting Exhaust Emissions: Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply the following species by the indicated factors:

isobutylene -- .53	methanol -- .23

For ethanol-blended CaRFG with 2 percent oxygen, adjust all species in proportion so that their sum is 97 percent and add 3 percent ethanol. Then, multiply the following species by the indicated factors:

benzene -- .96	1,3-butadiene -- .98
formaldehyde -- .94	acetaldehyde -- 1.27

For ethanol-blended CaRFG with 3.5 percent oxygen, adjust all species in proportion so that their sum is 94.7 percent and add 5.3 percent ethanol. Then, multiply the following species by the indicated factors:

benzene -- 1.00	1,3-butadiene -- .99
formaldehyde -- .92	acetaldehyde -- 2.32

In each profile, adjust (again) all species in proportion so that their sum is 100 percent.

Stabilized Exhaust: Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply the following species by the indicated factors:

isobutylene -- .53	methanol -- .49

For ethanol-blended CaRFG with 2 percent oxygen, adjust all species in proportion so that their sum is (100% - ethanol content) and add ethanol equal to 1.00 times the MTBE content of the ARB profile for MTBE-blended CaRFG. Then multiply the following species by the indicated factors:

benzene -- .96	1,3-butadiene -- .98
formaldehyde -- .94	acetaldehyde -- 1.27

For ethanol-blended CaRFG with 3.5 percent oxygen, adjust all species in proportion so that their sum is (100% - ethanol content) and add ethanol equal to 1.75 times the MTBE content of the ARB profile for MTBE-blended CaRFG. Then multiply the following species by the indicated factors:

benzene -- 1.00	1,3-butadiene -- .99
formaldehyde -- .92	acetaldehyde -- 2.32

In each profile, adjust (again) all species in proportion so that their sum is 100 percent.

Gasoline Composition: Remove MTBE from the ARB profile for MTBE-blended CaRFG (#419). Multiply the following species by the indicated factors:

n-butane -- .83	C5 and C6 paraffins -- .67
olefinic species -- .63	aromatic species except benzene -- .80
C7-C9 branched paraffins -- 1.85	

For ethanol-blended CaRFG with 2 percent oxygen, adjust all species in proportion so that their sum is 94.25 percent and add 5.75 (mass) percent ethanol. For ethanol-blended CaRFG with 3.5 percent oxygen, adjust all species in proportion so that their sum is 89.1 percent and add 10.1 percent ethanol.

Oxygen-Free CaRFG

Extended Diurnal Emissions: Remove MTBE from the ARB profile for MTBE-blended CaRFG. Adjust all species in proportion so that their sum is 100 percent.

Hot-Soak Emissions: Remove MTBE from the profile for MTBE-blended CaRFG. Adjust all species in proportion so that their sum is 100 percent. Multiply benzene by 1.06. Adjust (again) all species so that they sum to 100%.

Starting Exhaust Emissions: Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply isobutylene by .53. Adjust all species in proportion so that their sum is 100 percent. Multiply the following species by the indicated factors:

benzene -- .88	1,3-butadiene -- .98
formaldehyde -- .89	acetaldehyde -- .95

Adjust (again) all species in proportion so that their sum is 100 percent.

Stabilized Exhaust Emissions: Remove MTBE from the ARB profile for MTBE-blended CaRFG. Multiply isobutylene by .53. Adjust all species in proportion so that their sum is 100 percent. Multiply the following species by the indicated factors:

benzene -- .88	1,3-butadiene -- .98
formaldehyde -- .89	acetaldehyde -- .95

(Other changes may be appropriate but cannot be determined.) Adjust (again) all species in proportion so that their sum is 100 percent.

Gasoline Composition: Remove MTBE from the ARB profile for MTBE-blended CaRFG. Convert 80 percent of the existing butane content into butene. Multiply the following species by the indicated factors:

C5 and C6 paraffins -- 1.64	C7-C9 branched paraffins -- 1.99
aromatic species except benzene -- .74	

Adjust all species in proportion so that their sum is 100%.

CO Emissions

Increase the MVEI for gasoline-powered vehicles by 5 percent for oxygen-free CaRFG. Decrease it by 15% percent for ethanol-blended CaRFG with 3.5% oxygen. Leave it unchanged for ethanol-blended CaRFG with 2% oxygen.

Content

Recommended Profiles of Emissions for CaRFG w/o MTBE

(rev. 7/01/99)

Introduction

Table 1 lists ARB's emission profiles for CaRFG blended with MTBE and the studies on which the profiles are based. To give valid contrasts with these profiles, emission profiles for ethanol-blended and oxygen-free CaRFGs should be based on the same studies. That is, a new profile should be an adjustment of the corresponding profile for MTBE-blended CaRFG rather than be a totally new profile derived from another data source. A totally new profile would confound the effect of changing oxygenates with uncontrolled contrasts between sources in the hydrocarbon bases of their fuels, their test vehicles, and their laboratories.

Table 1. ARB's Profiles for CaRFG with MTBE

Profile	Source of Data
Gasoline (whole)	ARB, MTBE - EtOH study
Cat. stabilized exhaust	ARB, IUS*
Non-cat. stabilized exhaust	ARB, IUS
Cat. cold- & hot-start exhaust	ARB, IUS
Non-cat. cold- & hot-start exh	ARB, IUS
Extended diurnal	UC (Harley) head-space
Hot soak	ARB, MTBE - EtOH study^

* "In-Use Surveillance" ^ with alcohols removed

Except for gasoline and hot-soak emissions, the studies in Table 1 provide data for only the MTBE-blended CaRFG. However, there are other studies wherein both a CaRFG with MTBE and an ethanol-blended or oxygen-free CaRFG were tested in the same vehicles. They are shown in Table 2. We have used comparisons of speciations *within* one of more of these studies to determine whether and how to adjust each of the profiles in Table 1 to make it apply to an ethanol-blended or oxygen-free CaRFG. This approach approximates what each study in Table 1 *would have* measured for the other fuel.

Conceptually: (1) remove the oxygenates from both test profiles and the current ARB profile, (2) compute the ratio between the oxygen-free test profiles for each species to be adjusted, (3) adjust the species in the (oxygen-free) ARB profile by that ratio, (4) normalize to: [100% - appropriate ethanol content], (5) add the appropriate amount of ethanol**.** (Composition profiles of whole gasolines and the benzene, butadiene, formaldehyde, and acetaldehyde in emission profiles have been treated differently, as discussed near the end of this paper.)

Table 2. Studies with Speciated Emissions from Multiple CaRFGs

	ATL "Phase 1 - Phase 2"	**ARB** "MTBE - EtOH"	**Auto/Oil** Tech. Bull. 17
CaRFG types	MTBE, EtOH*	MTBE, EtOH*	MTBE, non-oxy.
Same HC base?	yes (both splashed)	yes (both splashed)	**
Fuel speciations?	no	yes	yes
Non-cat veh.?	no	no	no
Vehicle model years	Exh: '73 - '91 Evap: '78 - '91	1990 - 1995	1989, 1994
By-bag exh. data?	yes	yes	yes
Ext. DI data?	yes	yes	no
Hot-soak data?	yes	yes	yes
Comments	Alcohols & aldehydes not reported.	Excess C4 in DI; carry-over in DI & HS; combustion product in DI & HS	The two fuels were not matched in octane.

* RVP > 7 psi
** matched-RVP fuels; HC base of MTBE fuel was lower in C5 & C6 alkanes, higher in toluene

Each study in Table 2 has imperfections that complicate its use. The Auto/Oil work did not measure extended diurnal emissions. None of the studies used non-catalyst vehicles. The evaporative data from ARB's MTBE-EtOH test program has excessively high normal butane, due to the way the carbon cannisters were prepared. The ATL data do not include alcohols or aldehydes, which are the most important contrasting species between emissions from MTBE- and ethanol-blended fuels. (However, surrogate aldehyde data are available.) As splash-blended test fuels, the ethanol-blended fuels do not exactly reflect commercial fuels. Also, they were not true CaRFGs.* Finally, the ATL work did not include speciation of the gasolines, so that its emission profiles cannot be related to its gasoline compositions. However, the studies in Table 2 provide the only known speciation data that can be applied to estimating emission profiles. (Other kinds of information can be applied to estimating the compositions of gasolines and to the toxic species in the emission profiles. See "Toxic Species".)

* The EtOH-blended fuels did not meet the RVP limit at 7 psi. Also, they did not completely satisfy the Predictive Model. In particular, the ARB EtOH-blended fuel had a high oxygen content that caused a high NOx prediction.

Extended Diurnal Emissions -- EtOH-Blended CaRFG

The first step in determining the appropriate adjustment of the current profile of diurnal emissions is to compare the profiles for MTBE-blended gasolines in the ATL and ARB emission studies to the ARB's current profile for MTBE-blended CaRFG (#906). The latter is a head-space analysis for commercial gasoline samples taken during the Caldecott Tunnel sampling program. The comparison is in Figure 1, which shows the mean profile across all vehicles in tested each study. (For manageability, the figure shows just species that provided at least one percent to at least one profile. These species account for 84 to 90 percent of all the mass in each profile.)

In the figure, the data from the ARB's study have been adjusted in two ways. First, the fraction of n-butane has been fixed at 10 wt.%. An adjustment from the raw datum (48 wt.%) is required because it is known that some of the n-butane was an artifact from the test preparation of the carbon cannister. The value 10 wt.% was selected because it is equivalent to the n–butane value in the UC Caldecott profile, 6.29 wt.%, after adjustment via Raoult's law for the different n-butane contents of the ARB and UC fuels (1.01% / 0.63%). Second, the alcohol values in the ARB profile have been set to zero because they are presumed to be due to carry-over from emission runs with the ethanol-blended fuel (or some other contamination).

Figure 1 indicates that the ATL and ARB (adjusted) study profiles for extended diurnal emissions are each similar to the current (UC head-space) profile. Thus, it appears valid to use a comparison between the MTBE-and ethanol-blended fuels within either study to modify the current profile to reflect a change to ethanol.

(Note that the UC head-space profile is very poor in aromatic compounds compared to either of the actual diurnal profiles. This suggests that the UC head-space profile may need adjustment to properly portray diurnal emissions from MTBE-blended CaRFG.)

In Figure 1, the MTBE-blended profiles from the ARB and ATL studies are similar. However, the ATl profile is somewhat richer in aliphatic species and poorer in the aromatic species. Figure 2 shows that the same pattern for the ethanol-blended fuels: basically similar evaporative profiles with the ATL profile richer in alkanes. Since there is no speciation of the ATL fuels, we cannot tell if differences in the fuel compositions account for the different aliphatic/aromatic splits. The other possible explanation is a difference between test fleets in the effectiveness of the carbon cannisters according to species.

Figures 3 and 4 are the comparisons *within* each of the ATL and ARB data sets of the profiles for MTBE- and ethanol-blended CaRFGs. The ATL comparison is on the alcohol-free basis (no alcohol data). The ARB comparison is between profiles that (as discussed above) are each adjusted to 10 wt.% for n-butane and each rid of the ethanol or MTBE that was measured in the evaporative emissions but not present in the fuel.

In each figure, there is little difference between the two profiles except (in Figure 4) the switch in the oxygenate present and minor amounts of methanol and acetylene. (The latter are probably contaminants from the exhaust.) Some bars for the ethanol-blended fuel in the ARB "MTBE-EtOH comparison (Figure 4) are lower than their counterparts for the MTBE fuel. However, the oxygen content of the ethanol-blended fuel, 3.9 wt.%, exceeds the regulatory limit. Presumably, a lower oxygen content would reduce the ethanol bar and, thereby, increase all the other bars. Accordingly, there is not clear evidence of differences in diurnal emissions between MTBE- and ethanol-blended CaRFGs other than the identity of the oxygenate.

Therefore, it is recommended that the diurnal emission profile for MTBE-blended CaRFG be used also for ethanol-blended CaRFG except that the MTBE be replaced by an appropriate amount of ethanol. The only data for estimating that amount of ethanol are the ARB's MTBE- EtOH data, which apply to an ethanol content corresponding to 3.9 wt.% oxygen. The ethanol content in the (adjusted) profile is 21 wt.%. With the assumption that the mass of ethanol in the emissions is proportional to the oxygen in the fuel, Figure 4 shows how the ethanol bar would appear for oxygen at 2.0 or 3.5 wt.% oxygen. The appropriate ethanol contents are 11 percent and 19 percent, respectively.

<u>Hot-Soak Emissions -- EtOH-Blended CaRFG</u>

Figures 5 and 6 are analogues of Figure 1 and 2. Respectively, they compare the mean (over vehicles) profiles for the MTBE-blended fuels in the ATL and ARB studies and the profiles for the ethanol-blended fuels in the two studies. The two MTBE-blended profiles in Figure 5 are similar. The slight bias toward aliphatic species in the diurnal emission profile for the diurnal emissions (in Figure 1) is not evident here. However, in Figure 6, that bias is strong for the ethanol-blended fuels; the ATL profile is much richer in alkanes--especially isopentane--and poorer in aromatic species than is the profile from ARB's MTBE-EtOH study.

Table 3 shows the total aromatic, olefinic, and paraffinic contents of the hot-soak emissions from both fuels in both the ATL and ARB data sets, all on the oxygenate-free basis. There is very little difference between the two ARB fuels but substantial differences in the olefinic and aromatic contents of the emissions from the ATL fuels. Such a difference could have a substantial effect on the computed ozone formation in an air-quality model.

Table 3. Hot-Soak Compositions by Species Class
(Pct. of mass, oxygenate-free)

	ARB Data		ATL Data	
	MTBE fuel	EtOH fuel	MTBE fuel	EtOH fuel
Toluene	.173	.037	.142	.063
Total aromatic	.480	.483	.470	.140
Total olefinic	.041	.042	.060	.088
total paraffinic	.479	.476	.470	.772

The very high isopentane content of the hot-soak emissions from the ATL ethanol-blended fuel (average 31%) was seen in five of the six ATL test vehicles. These vehicles had much greater hot-soak emissions (by about 9 times) on the ethanol-blended fuel than on the MTBE-blended fuel. The hot-soak increase for the ethanol-blended fuel in the ARB study was much less. Although we do not know the isopentane contents of the ATL fuels, we know that they were both splash-blended into the same base. We conclude that failure of the carbon cannisters with the high-RVP ethanol-blended fuel--not fuel composition--caused the anomalous boost in the isopentane content of the hot-soak emissions.

Figures 7 and 8 are the comparisons within the ATL and ARB data sets, respectively, of the profiles for MTBE- and ethanol-blended CaRFGs. As for the diurnal profiles in Figure 3, the ATL comparison in Figure 7 is on the alcohol-free basis (no alcohol data). If, as in the ARB study (Figure 8), the actual ethanol content of the emissions was about one-third, each bar for the ethanol-blended fuel in Figure 7 should be reduced by about one-third for a direct comparison to its MTBE-blended counterpart. The comparison within the ARB data (Figure 8) is between profiles that are each rid of the oxygenate that was not part of the fuel. (No adjustment of butane was needed.)

Figure 7 indicates (with allowance for ethanol, as just discussed) that the ethanol-blended fuel in the ATL work produced hot-soak emissions distinctly poorer in aromatic species than did the MTBE-blended fuel. The aromatic contents are low (on the percent basis) mostly because the isopentane went so high when ethanol substituted for MTBE. As explained above, this is apparently an RVP effect (overwhelmed carbon cannister) that would not have occurred if the ethanol-blended fuel had met the CaRFG RVP limit. Thus, the profile in Figure 7 for the ethanol-blended fuel is not appropriate as a basis for adjusting the ARB's hot-soak emission inventory.

In Figure 8 (ARB data), no reduction of the aromatic content is evident in the profile for the ethanol-blended fuel. If the excess ethanol due to the unduly high ethanol content of the fuel (3.9 wt.% vs. 3.5 wt.% allowed or vs. 2.0 wt.% required by federal law) were distributed among the other bars in the graph, none of the aromatic contents (nor other classes) would remain notably poor in the ethanol-blended profile.

We also reviewed hot-soak speciation data from two other programs, which compared MTBE- and EtOH-blended gasolines that were not CaRFGs. In each program, the two fuels were splash-blended from the same base. However, neither program gives a comparison between 11% MTBE and 10% EtOH. Table 4 shows various statistics from the studies, including the ratios between fuels of the iso-paraffin contents and the aromatic contents of hot-soak emissions.

The work by API showed little change in either the iso-paraffin (i-C4 plus i-C5) or aromatic contents when ethanol replaced MTBE, but the ATL "Low-Oxygenates" study (done with the same vehicles as the "Phase 1- Phase 2" study) showed substantial increases in both. Thus, with regard to aromatic species, the API work agrees with the ARB's MTBE-EtOH study result (no change), but the ATL "Low-Oxy" result disagrees with the ARB result and contradicts the ATL Phase 1-Phase 2 result (decreased aromatic). The Low-Oxy results repeated the increased isoparaffins, although not as dramatically as in the Phase 1- Phase 2 profile.

Table 4. Hot-Soak Species Ratios in Non-CaRFG Studies
(based on mean profiles across vehicles)

Study	Vehicles #	Vehicles MY's	MTBE Fuel %MTBE	MTBE Fuel RVP	EtOH Fuel %EtOH	EtOH Fuel RVP	**Hot-Soak Ratio,** EtOH fuel : MTBE fuel	
							tot. i-paraf.	tot. arom.
API; "Non-FTP"	10	81-89	7.5	9.0	10	9.9	1*	.9 *
API; "Non-FTP"	10	81-89	15	9.1	10	9.9	1*	.9 *
							$i\text{-}C_5$	benz. tol.
ATL; "Low-Oxy"**	6	73-91	11	7.7	5.7	8.5	2.0	2.2 1.5

* data at 80 d.F; read from a graph ** same vehicles as "Phase 1-Phase 2"

The two ATL studies give inconsistent results for the effect on the aromatic content of switching from MTBE to ethanol, despite using the same vehicles. Also, the ATl Phase 1- Phase 2 work did not involve replicate hot-soak testing, whereas the ARB study replicated each hot-soak run. These considerations, the agreement between the ARB and API studies, and the apparent cannister break-through discussed above reinforce a recommendation to use the ARB "MTBE-EtOH" data to create the hot-soak emission profile for ethanol-blended CaRFG.

Therefore, it is recommended that the existing hot-soak profile for MTBE-blended CaRFG be used also for ethanol-blended CaRFG except that the MTBE be replaced by an appropriate amount of ethanol. (For an additional recommendation for benzene, see "Toxic Species".)

The only data for estimating that amount of ethanol are the ARB's MTBE-EtOH data, which apply to an ethanol content corresponding to 3.9 wt.% oxygen. The (adjusted) ethanol content in the profile is 35 wt.%. With the assumption that the mass of ethanol in the emissions is proportional to the ethanol in the fuel, Figure 8 shows how the ethanol bar would appear for oxygen at 2.0 or 3.5 wt.% oxygen. The appropriate ethanol contents are 18 percent and 31 percent, respectively.

Start Emissions, Catalyst Vehicles -- EtOH-Blended CaRFG

Figure 9 shows the "start" profiles (FTP bag 1 minus bag 3) for the MTBE-blended fuels in the ATL "Phase 1- Phase 2" and ARB ("MTBE-EtOH") studies. It also shows the ARB's current profile for MTBE-blended CaRFG (IUS, #977). (For manageability, the figure shows just species that provided at least one percent to at least one profile. These species account for about 77 percent of all the mass in each profile.)

The ATL Phase 1-Phase 2 work measured aldehydes and other oxygenates in the exhaust emissions, but only FTP-composite data on formaldehyde and acetaldehyde are extant. However, five of the six test vehicles were also used in an immediately preceding ATL study ("Low-

Oxygenate") in which complete speciation data are available for MTBE-blended and ethanol-blended fuels. (They were not CaRFGs.) We have inserted into the ATL profile in Figure 9 the formaldehyde and acetaldehyde data* from those five vehicles operated on fuel "O" in the earlier ATL study. Also, the ARB and IUS (#877) profiles in Figure 9 have been adjusted to remove the other oxygenates that are not reported in the ATL profile (species other than MTBE, formaldehyde, and acetaldehyde).

The ATL and ARB profiles in Figure 9 differ noticeably from the IUS profile in the contents of n-butane, n-pentane, 2,3-dimethylbutane, methylcyclopentane, 3-methylpentane, n-hexane, and isooctane. However, these compounds are all fairly low in reactivity. In the more reactive hydrocarbons shown in the plot--olefins and aromatics--the ATL and ARB profiles are quite similar to the IUS profile. Also, the IUS values for the two aldehydes are similar to the ARB values. The aldehyde values in the ATL profile are somewhat higher; but since they are only surrogate data, the difference is not surprising.

Figure 10 shows the starts profiles from the ethanol-blended fuels in the ATL and ARB studies. The formaldehyde and acetaldehyde elements of the ATL profile are surrogates from fuel "U" in the ATL "Low Oxygenate" study. The two profiles compare much as do the two MTBE-blended profiles in Figure 9. Despite some differences between each other and with the IUS profile, the MTBE-blended profiles in the two studies changed similarly when ethanol replaced the MTBE. Thus, it appears valid to use a comparison between the MTBE-and ethanol-blended fuels within either the ATL or ARB study to modify the current (IUS) profile to reflect a change to ethanol. (While the aldehyde values in the ATL profiles are suspect, they are not really germane because aldehydes are treated specially, as in "Toxic Species".)

Figure 11 shows the starts profiles for the MTBE- and ethanol-blended fuels in the ATL study. The profiles include the hydrocarbons that provided at least one percent to at least one profile plus the "grafted" formaldehyde and acetaldehyde contents. (There are no alcohol data.) Except for the presence of MTBE, extra formaldehyde, and extra isobutylene (2-methylpropene) in the MTBE-blended profile (all expected), the two profiles are essentially identical.

Figure 12 is the analogous plot for the ARB study. It reflects the actual measured profiles, without any adjustments. It shows formaldehyde, acetaldehyde, and the sum of all other aldehydes. As does Figure 11, it shows essentially identical profiles except for extra MTBE, formaldehyde, isobutylene, and methanol in the MTBE-blended profile and increased ethanol and acetaldehyde in the ethanol-blended profile.

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* The surrogate aldehyde data (mg/mi) were appended to the Phase 1-Phase 2 HC emissions by vehicle.

It is important to be accurate in quantifying the change in the formaldehyde and acetaldehyde contents of starts emissions between MTBE-and ethanol-blended gasolines. Unfortunately, Figures 11 and 12 do not agree well these changes. This is not surprising, given the different oxygen contents of the ethanol-blended fuels in the two studies. Another major difficulty is that neither study (nor any other study) contrasts oxygen contents within ethanol-blended fuels. We conclude that Figures 11 and 12 cannot provide adjustment factors for aldehydes for ethanol-blended CaRFGs. (Other means of creating the adjustments are described in "Toxic Species".)

Another important aspect of creating exhaust profiles for non-MTBE CaRFG is the adjustment factor the isobutylene content. Since the known dominant determinant of isobutylene emissions is the MTBE content of the fuel*, the adjustment is expected to be the same for all MTBE-free gasolines regardless of the presence of oxygen. Table 5 shows experimental data on the ratio of isobutylene between MTBE-free and MTBE-blended fuels, for both starting and stabilized (bag 2) emissions.

Table 5. Isobutylene Ratios, Non-MTBE Fuel:MTBE Fuel

	ARB, "MTBE-EtOH"	ATL, "Ph1- Ph2"	Auto/Oil, #6 (15% MTBE, not CaRFGs)	Auto/Oil, #17 (11% MTBE, both CaRFGs)
Starts (B1-B3)				
EtOH-blended	.47	.56	.59	xx
no oxygen	xx	xx	xx	.57
Stabilized (B2)				
EtOH-blended	.40	.46	no data	xx
no oxygen	xx	xx	xx	.68

For the starting emissions, the table shows no difference in the isobutylene ratio between ethanol-blended fuels and oxygen-free fuels. For the stabilized emissions, there may be a difference between the ratios for the ethanol-blended fuels and oxygen-free fuels. However, the mean of the three data, .51, is about the same as the mean of the four data for the starts ratio, .55. It seems reasonable to use .53 as the common value for adjusting the isobutylene content to create both exhaust profiles (starts and stabilized) for all the MTBE-free CaRFGs.

It is recommended that the existing starts (bag 1 - bag 3) profile for MTBE-blended CaRFG be used also for ethanol-blended CaRFG except that:

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* Butenes are other possible determinants, but their contents in CaRFG are too low to be effective.

- **the isobutylene content in the MTBE-blended profile be multiplied by .53**
- **the methanol content be multiplied by .23**
- **the MTBE be replaced by an appropriate amount of ethanol**.
- (Also, see "Toxic Species".)

The only data for estimating the amount of ethanol are the ARB's MTBE- EtOH data, which apply to an ethanol content corresponding to 3.9 wt.% oxygen. The ethanol content in the profile is 6 wt.%. With the assumption that the mass of ethanol in the emissions is proportional to the ethanol in the fuel, Figure 12 shows how the ethanol bar would appear for oxygen at 2.0 or 3.5 wt.% oxygen. The appropriate ethanol contents are 3 percent and 5.3 percent, respectively.

Stabilized Exhaust Emissions, Catalyst Vehicles -- EtOH-Blended CaRFG

Figure 13 shows the "stabilized exhaust" profiles (FTP bag 2) from the ATL "Phase 1-Phase2" and ARB ("MTBE-EtOH") studies, and it shows the ARB's current profile for MTBE-blended CaRFG (IUS, #876). We have used methane-free profiles because of large differences among the three data sources in the methane content of bag 2. (For manageability, the figure shows just species that provided at least two percent to at least one profile. These species account for about 73 percent of methane-free masses in the ATL and ARB profiles.) Figure 14 shows the EtOH-blended profiles from the two studies.

As with the starts profiles, we have inserted into the ATL profiles the bag-2 formaldehyde and acetaldehyde contents from fuels "O" (MTBE-blended) and "U" (EtOH-blended) in the ATL "Low-Oxy" study. Also, the ARB and IUS (#876) profiles have been adjusted to remove the other oxygenates that are not reported in the ATL profile (species other than MTBE, formaldehyde, and acetaldehyde).

In each of these figures, the ATl and ARB "MTBE-EtOH" profiles differ more than do their counterparts in the other emission elements. Also, the two MTBE-blended profiles differ noticeably from the ARB's current bag 2 profile (IUS). The variability in profiles may be due to differences in the effectiveness of the catalysts among vehicles in the two studies and the in-use fleet sample in the IUS. The high acetylene, high ethylene, and low ethane for the IUS profile indicate much poorer catalyst function relative to the ATl and ARB study vehicles.

The MTBE content of the ARB profile in Figure 13 is very low compared to both the ATL and IUS profiles. It is also very low compared to measurements by Harley in the Caldecott Tunnel (not shown here). Also, in Figure 14, the ethanol content of the ARB "MTBE-EtOH" profile is very low, inconsistent with observations in other work.

Despite the inconsistency between studies, Figures 15 and 16 show that within either study the profiles for the MTBE- and EtOH-blended fuels are similar. The most notable differences between profiles are those that are expected: more MTBE, isobutylene (2-methylpropylene), formaldehyde, and methanol in the profiles for the MTBE-blended fuels and more ethanol and acetaldehyde in the profiles for the ethanol-blended fuels. The only other notable differences between two profiles are in the ATL comparison (Figure 15), wherein toluene and o-xylene are richer in the ethanol-blended profile and 1,2,4-trimethylbenzene is poorer. However, Figure 16 does not corroborate these latter differences.

On the base of Figure 16 and the common adjustments for isobutylene developed in the section above, **it is recommended that the existing stabilized exhaust (bag 2) profile for MTBE-blended CaRFG be used also for ethanol-blended CaRFG except that:**

- **the isobutylene content in the MTBE-blended profile be multiplied by .53**
- **the methanol content be multiplied by .49**
- **the MTBE be replaced by an appropriate amount of ethanol**.
- (Also, see "Toxic Species".)

The only data on the ethanol content of bag 2 emissions, from the ARB's MTBE/EtOH study, are unrealistic. Therefore, in this case (only), the MTBE content in the existing stabilized exhaust (bag 2) profile for MTBE-blended CaRFG should be multiplied by the ratio of the ethanol and MTBE bars in Figure 16 (1.96) to give the ethanol content corresponding to 3.9% oxygen and then by 3.5/3.9 or 2.0/3.9 to provide the ethanol contents corresponding to 2 or 3.5 wt.% oxygen, respectively. The two resulting adjustment factors are 1.00 and 1.75.

<u>Non-Catalyst Vehicle Emissions -- EtOH-Blended CaRFG</u>

There are no speciation data within a single study for exhaust emissions from MTBE-and ethanol-blended CaRFGs in non-catalyst vehicles. The obvious recourse is to apply the above recommendations to the ARB profiles for non-catalyst vehicle emissions.

<u>Extended Diurnal Emissions -- Oxygen-Free CaRFG</u>

There are no data to compare diurnal emission species between an MTBE-blended CaRFG and an oxygen-free CaRFG. Therefore, the following recommendations for creating a hot-soak profile for oxygen-free CaRFG should be applied also to diurnal emissions.

<u>Hot-Soak Emissions -- Oxygen-Free CaRFG</u>

Only one study provides data comparing hot-soak emission profiles between MTBE-blended and oxygen-free CaRFGs, Auto/Oil <u>Technical Bulletin 17</u>. It is not ideal for the current purpose because the oxygen-free fuel had a lower value of (R+M)/2 than did the MTBE-blended fuel, by 2.5 numbers. (The MTBE-blended fuel had a very high (R+M)/2 : 92.5.) In actual production, an octane discrepancy between CaRFGs would be avoided by means that could affect the relative hot-soak profiles. If there would be "room" in the Predictive Model to adjust the aromatic content of oxygen-free CaRFG, the octane "trim" could be done with aromatic-rich blending materials. However, for the fuels predicted by MathPro in its recent linear-programming work for the Energy Commission, oxygen-free CaRFG has a *lower* aromatic content than does the MTBE-blended CaRFG; the octane replacement for MTBE is provided by increased blending of alkylates (branched alkanes). *Therefore, it is not clear how the* *compositional differences between the two Auto/Oil fuels(and their emission profiles) may be related to the contrasts between actual (future commercial) CaRFGs*. However, there are no other data.

Figure 17 compares the hot-soak profile from A/O fuel C2 (11.2% MTBE) to the ARB's current hot-soak profile, #420 (which is the "MTBE-EtOH" hot-soak profile with the alcohols removed). Only species providing at least one percent to at least one profile are plotted. Unlike all the previous plots in this paper, the plotted species account for notably different fractions of the total masses of the two profiles, 88% for the ARB profile but only 74% of the A/O C2 profile. Among these disparate fractions, most of the plotted species are richer in the ARB profile than in the A/O profile. However, if the bars in Figure 17 were normalized over just the plotted species, the profiles would be very similar except for MTBE. (That is, except for less MTBE in the A/O profile, the relative amounts of these more plentiful species would be about the same in the two profiles.)

Figure 18 compares the hot-soak profiles for A/O fuels C2 (11.2% MTBE) and C1 (no oxygen). They are similar except for the expected difference in the MTBE contents. (The presence of a little MTBE in the C1 profile probably represents carry-over from runs on MTBE-blended fuels.) Figure 19 shows the same profiles on the MTBE-free basis. It confirms that except for the absence of MTBE, the oxygen-free hot-soak profile is essentially the same as the profile for the MTBE-blended fuel. (This is despite compositional differences between the fuels, as shown in Table 6.)

Therefore, it is recommended that the hot-soak emission profile for MTBE-blended CaRFG be used also for oxygen-free CaRFG except that the MTBE be removed. (See "Toxic Species" for additional recommendations.)

<u>Start Emissions, Catalyst Vehicles -- Oxygen-Free CaRFG</u>

Figure 20 shows the current ARB profile (#877) of bag 1 - bag 3 emissions for MTBE-blended CaRFG and the profile for Auto/Oil fuel C2 (11.2% MTBE). (Auto/Oil does not report methanol.) The two profiles agree in general. The Auto/Oil profile is higher in propene, isobutene, and trimethylpentanes but lower in isopentane. The difference in isopentane is attributable to its different contents in the two fuels, and the differences in trimethylpentanes are partly attributable to the fuel contents.

Figure 21 shows the bag 1 - bag 3 profiles for the A/O MTBE-blended and oxygen-free CaRFGs (fuels C2 and C1). Besides the expected (near) absence of MTBE and lower isobutylene fraction in the oxygen-free profile, there are some differences in the mono- and di-substituted C4s and C5s and in toluene. However, the latter differences correspond almost exactly to differences in the fuel contents.

Since methanol was not reported by Auto/Oil, no fractional reduction from the MTBE-blended to oxygen-free profiles can be estimated. We will assume that methanol is completely removed from the profile.

The two profiles in Figure 21 do not differ in formaldehyde or acetaldehyde. This is surprising because formaldehyde is a known reaction product of MTBE. The Auto/Oil profiles are means over vehicles in three categories: the "current fleet"vehicles of the 1989 model year, the federal "Tier 1" vehicles, and "advanced technology" vehicles that were prototypes for production LEVs. Within these categories, the average profiles for the oxygen-free CaRFG had 6 percent greater, 8 percent lower, and 13 percent lower formaldehyde contents, respectively, than did the MTBE-blended CaRFG. While these numbers support reductions of the formaldehyde in the oxygen-free starts profile, the data do not allow quantitation of the effect. (However, see "Toxic Species".)

Accordingly, it is recommended that the existing starts (bag 1 - bag 3) profile for MTBE-blended CaRFG be used also for oxygen-free CaRFG except that the methanol and MTBE contents be eliminated. (Also, see "Toxic Species".)

Stabilized Exhaust Emissions, Catalyst Vehicles -- Oxygen-Free CaRFG

Figure 22 shows the current ARB profile (#876) for bag 2 exhaust from MTBE-blended CaRFG and the Auto/Oil counterpart (fuel C2). They are very different. Figure 23 shows the same profiles on the methane-free basis, where they are still very different. In the ARB profile, the low methane and ethane and the high acetylene, ethylene, and formaldehyde all indicate poor catalyst performance for the IUS vehicles compared to the Auto/Oil vehicles. This difference in the vehicle behaviors in the IUS and Auto/Oil programs raises a doubt about the validity of modifying the IUS bag 2 profile according to contrasts between the Auto/Oil fuels.

Figure 24 shows the bag 2 profiles for the A/O MTBE-blended and oxygen-free CaRFGs (fuels C2 and C1). The methane contents are very similar. Figure 25 shows the profiles methan-free (for better resolution of other species). As expected, the profile for the oxygen-free fuel has less MTBE (essentially zero) and isobutylene (by 32%) than does the profile for the MTBE-blended fuel. The oxygen-free profile also has greater C_4 to C_6 alkane contents, which can be explained in part by the greater contents of those species in the Auto/Oil oxygen-free fuel (averaging 50% over the contents in the MTBE-blended fuel). However, the oxygen-free profile also has lower contents of C_8 and higher aromatic species, even though the oxygen-free fuel had *higher* contents of virtually all such species than did the MTBE-blended fuel.*

It is of interest to look more closely at the differences in the emission profiles in light of the differing compositions of fuels C1 and C2. Unlike the fuel pairs used to develop the profiles

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* The FIA measurement of total aromatic content (vol.%) is greater for the MTBE-blended fuel (C2) than the oxygen-free fuel, but almost all the "GC aromatics" (wt.%) are more abundant in the latter fuel, with toluene being the only notable exception. The FIA method is imprecise.

for ethanol-blended CaRFG, fuels C1 and C2 did not have the same hydrocarbon base. Table 6 lists for both the emissions and the fuels the contents of the C4+ hydrocarbons that are included in Figure 25. Also, it shows the percent differences between the two Auto/Oil bag-2 profiles when the contents of each species in the profiles have been normalized to a constant content in the fuels. (Each value in the oxygen-free fuel's emission profile is multiplied by the ratio of the species content in the MTBE-blended fuel to its content in the oxygen-free fuel.) This normalization attempts to account for the emission effects of differing fuel contents, but it is an over-correction because not all of an emitted species derives directly from the fuel.

Table 6. A/O Bag 2 Profile Differences Adjusted by Fuel Contents

	Profiles, wt.%		Fuel Contents, wt.%		Profile Diff., % of MTBE	
	MTBE	no oxy.	MTBE	no oxy.	actual	adjusted*
i-butane ^	.601	.665	.097	.109	10.6	-1.5
n-butane ^	1.11	2.55	1.66	1.72	130	122
i-pentane (C5's)	2.42	3.70	7.00	8.96	52.9	19.4
n-pentane	.417	.774	1.07	1.46	85.6	36.0
n-hexane	.476	.487	1.03	1.07	2.3	-1.5
2M-pentane (C6's)	1.26	2.05	3.92	6.76	62.7	-5.7
3M-pentane	.631	.910	2.12	3.24	44.2	-5.6
2,3-DM-butane	.644	1.02	1.49	2.86	58.4	-17.5
2,3-DM-pentane	1.2	1.19	4.17	4.93	-0.8	-16.1
2,4-DM-pentane	.79	.856	2.36	2.37	8.4	7.9
2,2,4-TM-pentane	3.18	3.60	9.01	10.0	13.2	2.0
2,3,3-TM-pentane	.61	.623	2.61	2.89	2.1	-7.8
2,3,4-TM-pentane	.757	.757	2.61	2.89	0.0	-9.7
benzene	1.29	1.20	1.26	1.2	-7.0	-2.3
toluene	1.91	1.70	7.86	5.09	-11.0	37.4
ethylbenz. (C8,9)	.68	.519	2.37	3.18	-23.7	-43.1
m- & p-xylene	1.8	1.43	5.29	6.77	-20.6	-37.9
o-xylene	.667	.504	1.77	2.24	-24.4	-40.3
1,2,4-TM-benzene	1.21	.764	1.82	1.89	-36.9	-39.2
1M,3E-benzene	.707	.457	1.28	1.42	-35.4	-41.7
1,2,3,5-TM-benz ^	.831	.351	.159	.189	-57.8	-64.5

* computed from profile contents normalized to a common fuel content for the species
^ probably not predominantly fuel-derived

Since the bag-2 profile contents of the butanes and the 1,2,3,5-tetramethylbenzene exceed their fuel contents, they are likely to not be predominantly derived from the fuel (unburned material). Therefore, their values in the right-most column of the table (fuel-normalized difference between profiles) may be disregarded. For the other species, the right-most column probably has some meaning, although as stated above, its derivation is an over-correction for the fuel composition's influence on the relative amounts of the species in the emission profiles. The best estimate for the difference in bag 2 profiles *if the fuels C1 and C2 had the same hydrocarbon base* is probably something intermediate to the two right-most columns. Thus, there are some obvious differences between the "propensities" for the two Auto/Oil fuels to put certain species in bag 2. Roughly, these may be:

C5 alkanes: +40% branched C6 alkanes: + 25% benzene: -5%
toluene: + 15% C8, C9 aromatics: -35%

However, given that (1) the IUS and Auto/Oil bag 2 profiles for MTBE-blended CaRFG differ strongly and (2) the Auto/Oil fuels have an unrealistic contrast in octane (and, therefore, in hydrocarbon composition), it is not at all clear what quantitative adjustments would be appropriate for the IUS bag 2 profile to turn it into a profile for oxygen-free CaRFG. Accordingly, although Figure 26 and Table 6 indicate that the starts profiles are likely not the same for MTBE-blended and oxygen-free CaRFGs, no changes in the hydrocarbon species of the bag 2 profile can be recommended on the basis of the available data.

In addition to the differing hydrocarbon contents, Figure 25 shows for the oxygen-free fuel a 13 percent decrease in the formaldehyde content, a 27 percent decrease in acetaldehyde content, and a 62 percent increase in other aldehydes. The reduction in the formaldehyde is expected because it is a known decomposition product of MTBE, and the 13% figure is commensurate with results from the ARB's Predictive Model. (See Table 13). The changes in the other aldehydes are not explained. (See "Toxic Species".)

Accordingly, it is recommended that the existing stabilized exhaust (bag 2) profile forMTBE-blended CaRFG be used also for oxygen-free CaRFG except that the methanol and MTBE contents be eliminated (Also, see "Toxic Species".)

Composition of CaRFG Blended with Ethanol

As with the emission profiles, the contrasts in composition among CaRFGs blended with MTBE, with ethanol, and without oxygenates should be reflect a common base. That is, the ARB speciation profile for MTBE-blended CaRFG should be modified to reflect what the same gasoline would have been had it come from the same source but been blended with ethanol or without any oxygenate. Given that the current ARB profile for MTBE-blended CaRFG (#419) is the composition of the MTBE-blended test fuel in the ARB's MTBE/EtOH test program, there are three possible ways to approximate the corresponding hypothetical ethanol-blended CaRFG:

1. Adjust the composition of the ethanol-blended test fuel in the same program so that the adjusted fuel would have been a true CaRFG. (The ethanol-blended test fuel was splash-

blended into the same hydrocarbon base as was the MTBE-blended test CaRFG.)

2. Adjust profile #419 according to the differences between the MTBE- and ethanol-blended CaRFGs "produced" by MathPro's linear-programming model in the CEC-sponsored study of the effects of banning MTBE.

3. Adjust the composition of the splash-blended ethanol fuel in the ATL Phase 1-Phase 2 test program so that it would approximate a true CaRFG; then adjust profile #419 according to the differences between the MTBE- and adjusted ethanol-blended fuels in the ATL study.

The first two approaches are developed below. The third approach would use a hybrid of the techniques in the first two, thereby involving the error potentials of each; therefore, it has not been developed.

Table 7 shows the regulated properties of the ARB test fuels and the modeled fuels in the CEC/MathPro work. Note that the ARB's ethanol-blended test fuel had a greater aromatic content than did the MTBE-blended test fuel, while MathPro predicted that ethanol-blended CaRFG would have a lesser aromatic content than does MTBE-blended CaRFG. Also, the relative T50's of the two types of fuel are reversed between the two sources.

Table 7. Values of Regulated Properties

	ARB Test Fuels		MathPro's Modeled CaRFGs	
	MTBE-blended	EtOH-blended	MTBE-blended*	EtOH-blended**
RVP	6.9	7.8	6.8	5.5 + 1.3
Oxygen	2.09	3.94	2.1	2.7
Olefinic	5.2	5.2	4.3	2.9
Aromatic	23.4	26.5	24	20.4
Sulfur	32	33	24	25
T50	197	186	200	206
T90	296	297	307	300
Benzene	.81	.82	.67	.80

* Ref. 2002, 1, CARB ** BAS U, alk-100, 1, CARB
(Data from "Refinery Modeling Task 3", Exhibit 8, intermediate term, flat-limit Predictive Model)

Adjusting ARB's EtOH Test Fuel. The composition the ethanol-blended test fuel is given by ARB profile # 418. The test fuel was not a CaRFG because it contained more than the allowed oxygen content (3.9 wt% vs. 3.5 wt.% allowed), the NOx prediction by the Predictive Model exceeds the criterion (3.5% increase vs. 0.04% allowed), and the RVP was too high (7.8 psi vs. 7.0 allowed). According to the Predictive Model, the following property changes would have made it a CaRFG with 2.0 and 3.5 wt.% oxygen:

	3.94% O	--->	2.0% O	3.5% O	
RVP	7.8	--->	7.0	7.0	(all other properties
sulfur	33	--->	33	20	constant)
olefins	5.2	--->	5.2	2.0	

Apparently, then, the only differences in the hydrocarbon makeup needed to convert the ethanol-blended test fuel into a CaRFG would be an adjustment to reduce the RVP and, in the case of oxygen at 3.5%, a small change in the olefinic content. (Reducing the sulfur content could also affect hydrocarbons, but the effect is not known.) Note that the two adjusted oxygen and olefinic contents bracket those in MathPro's predicted ethanol-blended CaRFG (in Table 7).

The total C4 content of the ethanol-blended test fuel was 1.21 wt.%, and the total C5 content (mostly isopentane) was 13.4%. Using blending RVPs of 20 psi for mixed C5s and 68 psi for mixed C4s, one calculates that by removing all C4s and 0.7 wt.% isopentane, the RVP would be reduced to 6.9 psi.

Thus, according to this approach, composition profile #418 (EtOH test fuel) with the C4s and lighter species removed, the isopentane content reduced by 0.7 wt.%, the ethanol content multiplied by 2.0/3.94, and re-normalization to 100% would be the composition profile for ethanol-blended CaRFG containing 2.0 weight percent oxygen. To reflect 3.5% oxygen, the C4s and C5s would be changed as noted, the ethanol content would be multiplied by 3.5/3.94, and the total olefinic content would then be adjusted to 2.0 vol.%.

Adjusting Profile #419 (MTBE-blended CaRFG) via MathPro Predictions. Table 8 shows the available detail on the composition of the CaRFGs predicted by MathPro. According to this approach, the n-butane content in profile #419 would be multiplied by .54/.65, the C5 and C6 paraffins would be multiplied by 4.6/6.9, the C7-C9 branched paraffins would be multiplied by 30.1/16.3, the aromatic contents other than benzene would be multiplied by 21.7/27.1, benzene by .87/.76, the olefinic contents 3.1/4.9, and the MTBE would be replaced by ethanol in the amount 16/46 *2 = 5.75 or 16/46 * 3.5 = 10.1 percent ethanol.

This second approach involves considerably more change to profile #419 than the first approach would change the ethanol-blended test fuel composition. It has the advantage of using a prediction of commercially produced ethanol-blended CaRFG (as opposed to a splash-blended test fuel) but the disadvantage of an incomplete comparison between the ethanol- and MTBE-blended fuels. Although incomplete, the comparison between predicted fuels conforms to

Table 8. Compositions of CaRFGs Modeled by MathPro (vol.%)

	MTBE-Blended*		EtOH-Blended**	
	actual	w/o MTBE	actual	w/o EtOH
n-Butane	.6	.65	.5	.54
C5's &C6's (paraffins)	6.1	6.9	4.3	4.6
Alkylate (branched C7, C8, C9 paraffins)	14.4	16.3	28.4	30.1
Benzene	.67	.76	.80	.87
Total aromatic	24	27.1	20	21.7
Total olefins	4.3	4.9	2.9	3.1
Oxygenate	11.4	--	7.8	--
Other	39	43	35	38
Oxgyen (wt.%)	2.1	--	2.7	--

* Ref. 2002, 1, CARB ** BAS U, alk-100, 1, CARB

statements from refiners about how they would have to change their gasolines to admit ethanol. The changes include significant removal of pentanes and an increased use of alkylates--neither of which are reflected in the adjustment of the ARB's ethanol-blended test fuel, as described above. Therefore, the second approach--modifying ARB's profile #419 for MTBE-blended CaRFG--is generally preferred for creating the contrasting profile for ethanol-blended CaRFG.

However, the MathPro predictions include benzene contents for all future CaRFGs greater than the average in today's gasoline. Upcoming regulatory changes likely will prevent such an increase. There is not an adequate basis for predicting a contrast in the benzene contents of future CaRFg types. Therefore, it is recommend to make no adjustments to the benzene content in the profile for MTBE-blended CaRFG (except as must occur by normalization).

Accordingly, it is recommended that ARB profile #419 be used to represent ethanol-blended CaRFG except that:

- **the C4 content be multiplied by .54/.65**
- **the C5 and C6 paraffins in oxygen-free profile #419 be multiplied by 4.6/6.9**
- **the C7-C9 branched paraffins (oxygen-free) be multiplied by 30.1/16.3**
- **all aromatic species (oxygen-free) except benzene be multiplied by 21.7/27.1**
- **the olefinic contents (oxygen-free) be multiplied by 3.1/4.9**
- **the MTBE be replaced by ethanol in the amount 5.75 percent for 2.0% oxygen**

and in the amount 10.1 percent for 3.5% oxygen.

Composition of Oxygen-Free CaRFG

ARB profile #419 is to be adjusted to reflect CaRFG blended without oxygen. One possible approach would be to transfer to profile #419 the contrasts between Auto/Oil CaRFGs C2 and C1 However, the oxygen-free fuel (C1) had an (R+M)/2 2.5 units lower than that of the MTBE-blended fuel. This difference is unrealistic for commercial gasoline. Therefore, in conformity with the approach for ethanol-blended CaRFG, we are using a comparison between CaRFGs predicted by MathPro (but with constant benzene) to adjust #419 to reflect oxygen-free CaRFG. Table 9 shows the available detail on the fuels predicted by MathPro.

Table 9. Compositions of Modeled CaRFGs (vol.%)

	MTBE-Blended*		No Oxygen**
	actual	w/o MTBE	
Butenes	0	0	.4
n-Butane	.6	.68	.1
C5's &C6's (paraffins)	6.1	6.9	11.3
Alkylate (branched C7, C8, C9 paraffins)	14.4	16.3	32.5
Benzene	.67	.76	.80
Total aromatic	24	27.1	20
Total olefins	4.3	4.9	5.0
Oxygenate	11.4	--	0
Other	39	43	30

* Ref. 2002, 1, CARB ** 1, CARB

According to this data, **it is recommended that ARB profile #419 be used to represent oxygen-free CaRFG except that:**

- **the C5 and C6 paraffins in oxygen-free profile #419 be multiplied by 11.3/6.9**
- **the C7-C9 branched paraffins (oxygen-free) be multiplied by 32.5/16.3**
- **all aromatic species (oxygen-free) except benzene be multiplied by 21.7/27.1**
- **the MTBE be eliminated.**

Toxic Species

In the ATl Phase 1-Phase 2 study and in the ARB's MTBE-EtOH study, each fuel of the pair was blended from the same hydrocarbon base. Therefore, one expects a common content for most specific species in the two profiles within each of those studies. Table 10 generally confirms this for benzene and butadiene. (Formaldehyde and acetaldehyde in the two studies have already been discussed.)

Table 10. Benzene and 1,3-Butadiene in ARB and ATL Emissions

		Extended DI	Hot-Soak	Bag 1-Bag 3	Bag 2
		1,3-Butadiene			
ARB	MTBE			.62	.17
	EtOH (3.9% O)			.53	.16
ATL	MTBE			.67	.2
	EtOH (2% O)			.7	.2
		Benzene			
ARB	MTBE	1.52	3.03	2.77	4.51
	EtOH (3.9% O)	1.50	2.47	2.76	4.50
ATL	MTBE	1.7	3.58	3.27	2.3
	EtOH (2% O)	1.6	1.05*	3.5	2.7

* apparent cannister failure; not representative of CaRFG emissions

The only large and consistent effect in the table is in the hot-soak benzene. However, the hot-soak emissions from the ATL ethanol-blended test fuel cannot be used to represent emissions from ethanol-blended CaRFG (as discussed in the section on hot-soak profiles). In the ARB study, the benzene content of the hot-soak emissions was 19 percent lower for the ethanol-blended fuel than the MTBE-blended fuel. This contradicts the model used by USEPA and proposed in 1998 by ARB for estimating the effects of RVP and oxygen content on the benzene fraction of hot-soak emissions. For the fuels in the ARB study, the model predicts about equal benzene fractions for the two fuels.

We should not rely on the comparisons of test fuels in Table 10 to estimate the amounts of toxic species in emissions. The amounts of specific species are sensitive to gasoline properties such as the ethanol and benzene that are not necessarily realistic in the test fuels. Information based on more realistic fuel contrasts and more emission testing should be considered.

The appropriate profile adjustments for benzene and butadiene can be estimated with the ARB's Predictive Model using as inputs the properties of the CaRFGs predicted by MathPro (with benzene held constant). The Predictive Model estimates are based on a database much greater than the ARB and ATL test studies. MathPro's predicted fuels reflect the interaction of the CaRFG regulations with actual refineries in California. Using the MTBE-blended CaRFG as the baseline, one can predict the changes in benzene/THC and butadiene/THC for MathPro's oxygen-free CaRFG and ethanol-blended CaRFGs. For the latter, the 2.7 wt.% oxygen in the actually predicted fuel must be replaced with 2.0 and then with 3.5 wt.%.

Since the Predictive Model was developed mostly with data from oxygen-free or MTBE-blended gasolines, it should not be used to predict aldehyde emissions for gasolines with ethanol. Therefore, we have re-regressed the database to construct new models for acetaldehyde and formaldehyde that distinguish between ethanol and MTBE as the source of oxygen. Applied to the MathPro fuels, these new models predict changes in acetaldehyde and formaldehyde for the oxygen-free and ethanol-blended CaRFGs relative to the MTBE-blended CaRFG.

The differences in evaporative benzene fractions among the MathPro fuels (with benzene held constant) can be can be predicted with models we have derived using the functional forms in USEPA's "Complex Model" for RFG emissions. These models are:

diurnal & resting -- B/HC = (2.949 - 0.176 * RVP) * %B/100

hot-soak -- B/HC = (4.631 - 0.272 * RVP - 0.0144 * %MTBE) * %B/100

where %MTBE and %B are the MTBE and benzene contents (volume basis) of the fuel. (Note that these models are proportional to the benzene content of the fuel, which is being set constant here. Note also that removing MTBE increases the benzene fraction of hot-soak emissions.)

Tables 11 through 13 show the results of these methods just described. They corroborate Table 10 in the negligible changes in the butadiene fraction for the ethanol-blended CaRFG, and they show a similar result for oxygen-free CaRFG. However, unlike the Table 10 numbers, there is an increase in the hot-soak benzene fraction. For the oxygen-free CaRFG, exhaust benzene is 12 percent lower than for the MTBE-blended fuel, formaldehyde is 11 percent lower, and acetaldehyde is 5 percent lower. For the ethanol-blended CaRFGs, formaldehyde is reduced slightly, while acetaldehyde increases strongly with increased ethanol content.

Table 11. Modeled Changes in Evaporative Benzene Fractions
(benzene / HC)

Contrasting CaRFG*	Hot-Soak^	Diurnal^
no oxygen	+6%	0
EtOH, any oxygen content	+6%	0

* fuel predicted by MathPro; contrasted with MathPro's MTBE-blended CaRFG
^ at constant benzene content in the fuels

Table 12. Modeled Changes in Exhaust Benzene and Butadiene Fractions
(from Predictive Model; FTP-composite predictions for Tech 4)

Contrasting CaRFG*	Δ HC (%)	Δ Benz. (%)	Δ (Benz/HC) (%)**	Δ1,3BD (%)	Δ (BD/HC) (%)**
no oxygen	+1.2	-11	**-12**	-.8	**-2**
EtOH, 2% O	+0.9	-3.3	**-4**	-2.3	**-2**
EtOH, 3.5% O	-1.1	-.8	**0**	-2.3	**-1**

* fuel predicted by MathPro; contrasted with MathPro's MTBE-blended CaRFG
** approximation: $\Delta(A/B) / (A/B) = \Delta A / A - \Delta B / B$

Table 13. Modeled Changes in Aldehydes
(from new, oxygenate-specific models)

CaRFG*	Δ HC**	Δ Form. (%)	Δ (Form/HC) (%)	Δ Acet. (%)	Δ (Acet/HC) (%)
no oxygen	+1.2	-10	**-11**	-4	**-5**
EtOH, 2% O	+0.9	-5	**-6**	+28	**+27**
EtOH, 3.5% O	-1.1	-9	**-8**	+133	**+132**

* fuel predicted by MathPro; contrasted with MathPro's MTBE-blended CaRFG
** from the Predictive Model

Therefore, in addition to changes recommended elsewhere in this paper, it is recommended that these adjustments be made:

	Benzene, hot-soak	Benzene, exhaust	1,3-Butadiene	Formal-dehyde	Acetal-dehyde
No oxygen	1.06	.88	.98	.89	.95
Ethanol, 2% O	1.06	.96	.98	.94	1.27
Ethanol, 3.5% O	1.06	1.0	.99	.92	2.32

Since normalization of an adjusted profile to sum to 100% alters the individual species values and since the import of the four toxic species values is high, the normalization should be done before the adjustment factors are applied. Re-normalization will be needed after they have been applied.

<u>CO Emissions</u>

The oxygen content is accepted as the dominant gasoline variable in determining CO emissions (as long as some vehicles have periods of rich operation). Table 14 summarizes empirical information on CO versus oxygen content. There are the ARB's "MTBE-EtOH" study, wherein both the oxygen and RVP varied, and the constant-RVP contrasts in the Auto Oil "Technical Bulletin 6" data.

Table 14. Test Results on CO Emissions

	Experimental Comparisons	Diff. in CO, (stat. model)	$\Delta CO/\Delta O$ (%/%)
Auto/Oil #6 1989 vehicles	Oxygen-free gasolines & gasolines with 2.7 wt.% O; not CaRFGs, not common HC bases Contrasts at RVP = 8.0 & 8.8 psi	MTBE: -9.3% ETBE: -14.6%	-3.4 -5.4
ARB "MTBE-EtOH"	MTBE fuel: RVP = 6.8, 2.09 wt.% O EtOH fuel: RVP = 7.8, 3.94 wt.% O common HC bases	-10%	-5.4
ATL "Low Oxy."	Oxygen-free gasoline & 11% MTBE; common HC bases Contrast at RVP = 7.6 psi	twc/al **: twc/n-al ^: non-catalyst:	-1 -7.5 -40

* nominal ** 3-way catalyst, adaptive learning ^ 3-way cat., no adaptive learning

On the basis of this data, we recommend assuming a 5-percent decline in the CO inventory per weight-percent oxygen in the fuel. This is commensurate with the observed change in ambient CO when the winter oxygen program began. Since the vehicular emission inventory is based on CaRFG with 2 wt.% oxygen, the CO inventory for oxygen-free CaRFG would be ten percent greater. For ethanol-blended CaRFG, the inventory would be the same for the oxygen content at 2 wt.% and 15 percent less for the oxygen content at 3.5 wt.%.

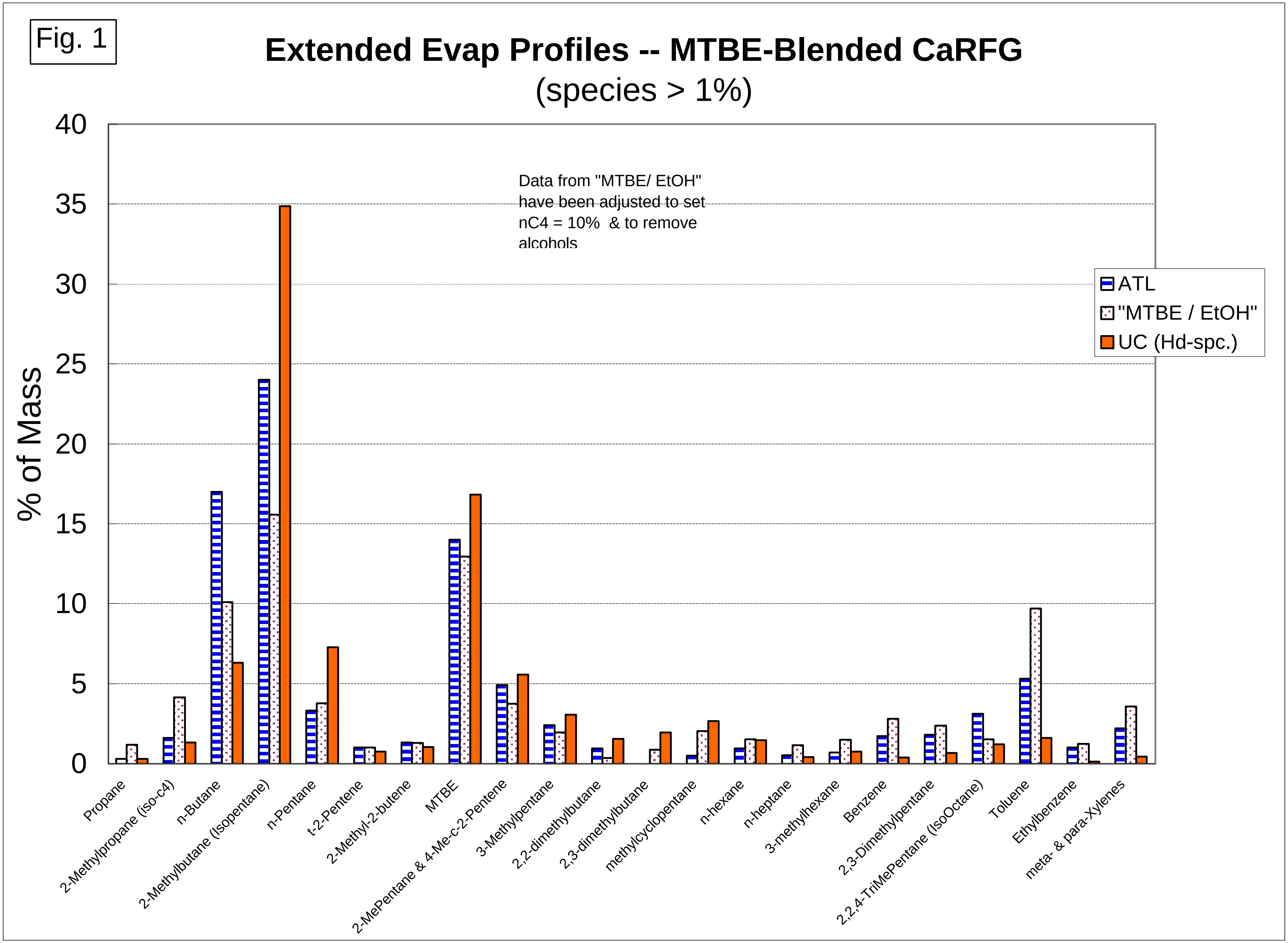


Fig. 1
Extended Evap Profiles -- MTBE-Blended CaRFG
(species > 1%)
% of Mass
0
5
10
15
20
25
30
35
40
Data from "MTBE/ EtOH" have been adjusted to set nC4 = 10% & to remove alcohols
ATL
"MTBE / EtOH"
UC (Hd-spc.)
Propane
2-Methylpropane (iso-c4)
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
t-2-Pentene
2-Methyl-2-butene
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
2,2-dimethylbutane
2,3-dimethylbutane
methylcyclopentane
n-hexane
n-heptane
3-methylhexane
Benzene
2,3-Dimethylpentane
2,2,4-TriMePentane (IsoOctane)
Toluene
Ethylbenzene
meta- & para-Xylenes

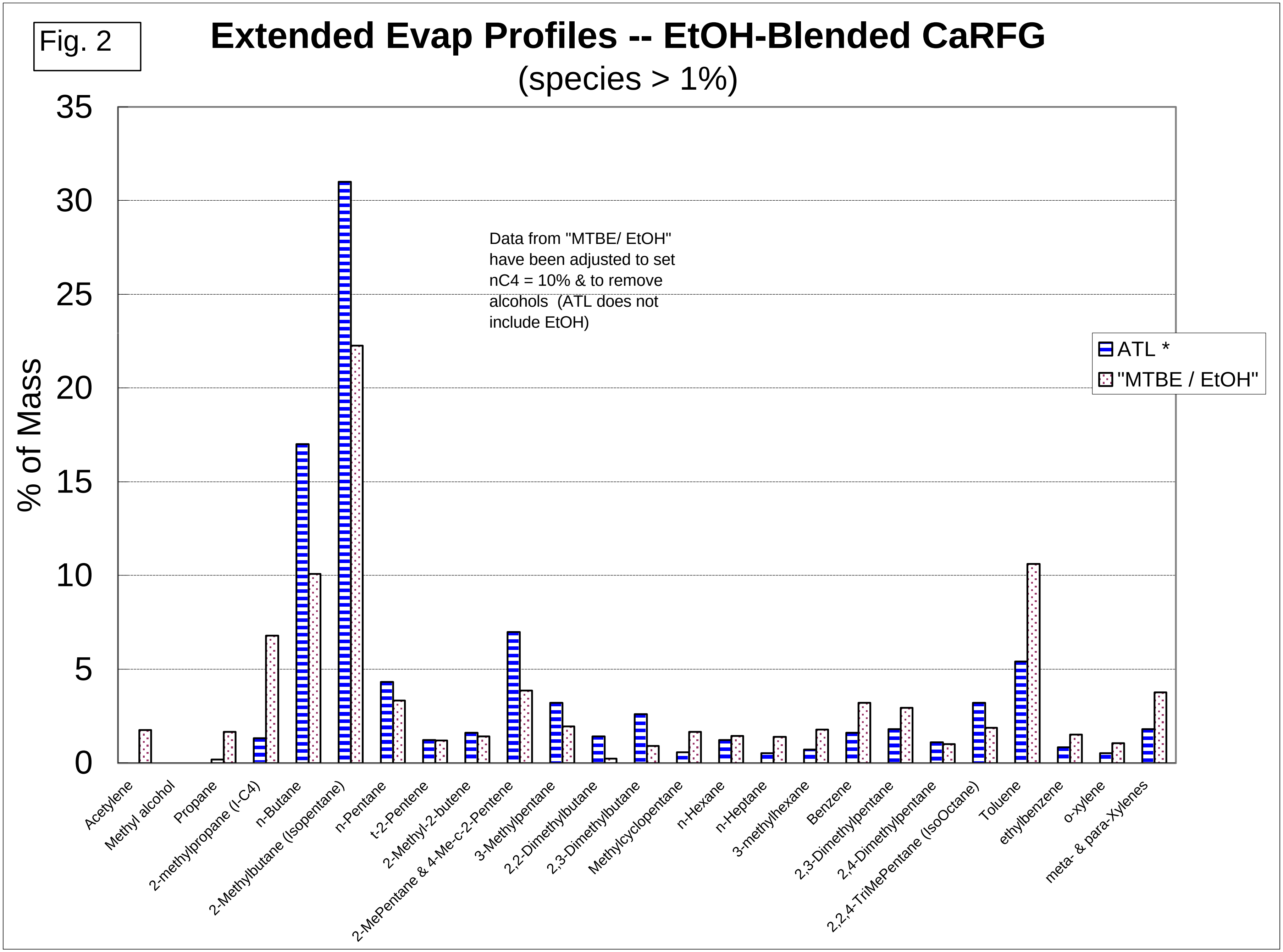
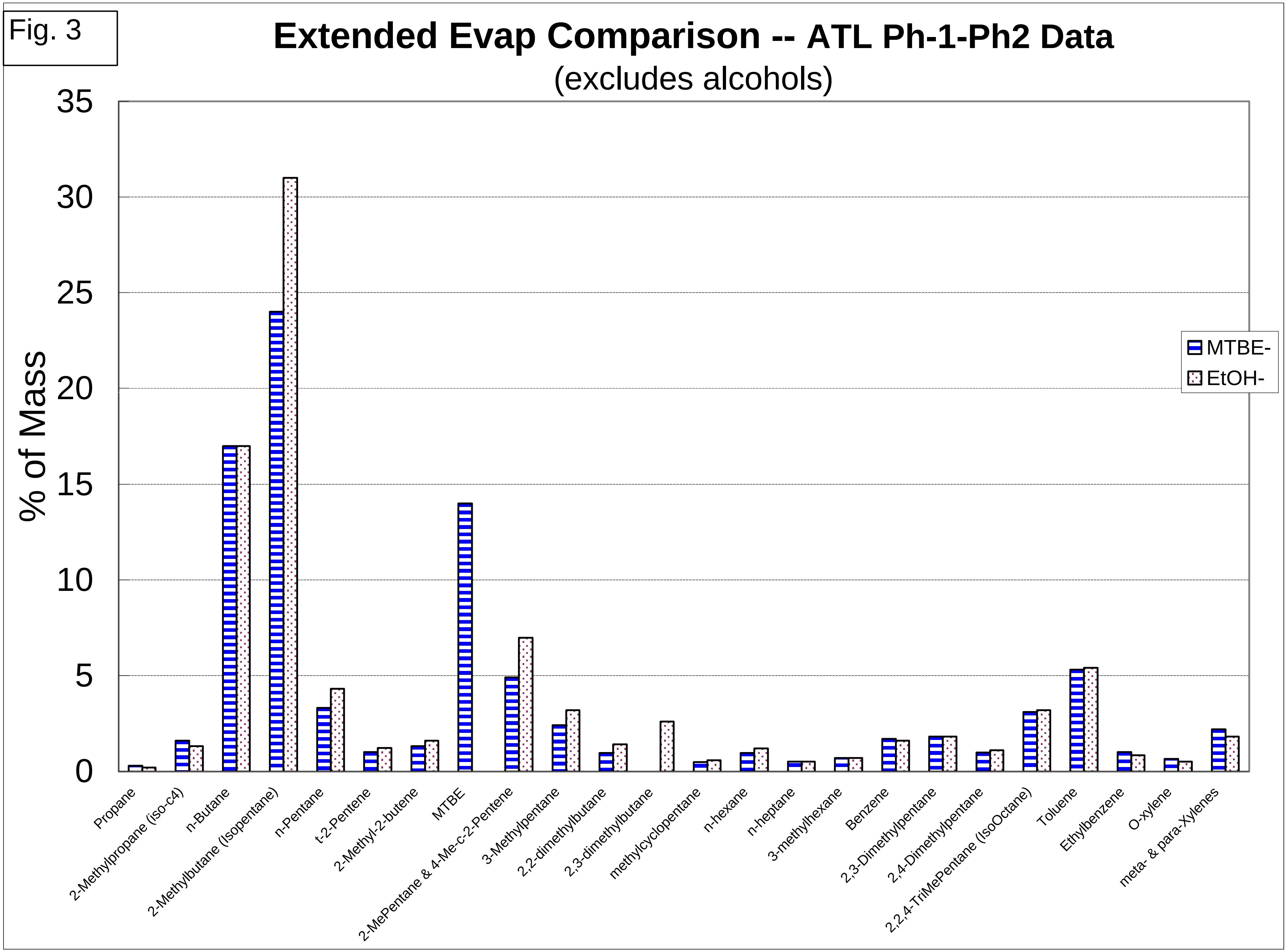


Fig. 2
Extended Evap Profiles -- EtOH-Blended CaRFG
(species > 1%)
% of Mass
0
5
10
15
20
25
30
35
Data from "MTBE/ EtOH" have been adjusted to set nC4 = 10% & to remove alcohols (ATL does not include EtOH)
ATL *
"MTBE / EtOH"
Acetylene
Methyl alcohol
Propane
2-methylpropane (I-C4)
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
t-2-Pentene
2-Methyl-2-butene
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
2,2-Dimethylbutane
2,3-Dimethylbutane
Methylcyclopentane
n-Hexane
n-Heptane
3-methylhexane
Benzene
2,3-Dimethylpentane
2,4-Dimethylpentane
2,2,4-TriMePentane (IsoOctane)
Toluene
ethylbenzene
o-xylene
meta- & para-Xylenes

Fig. 3


Extended Evap Comparison -- ATL Ph-1-Ph2 Data
(excludes alcohols)
% of Mass
0
5
10
15
20
25
30
35
MTBE-
EtOH-
Propane
2-Methylpropane (iso-c4)
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
t-2-Pentene
2-Methyl-2-butene
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
2,2-dimethylbutane
2,3-dimethylbutane
methylcyclopentane
n-hexane
n-heptane
3-methylhexane
Benzene
2,3-Dimethylpentane
2,4-Dimethylpentane
2,2,4-TriMePentane (IsoOctane)
Toluene
Ethylbenzene
O-xylene
meta- & para-Xylenes

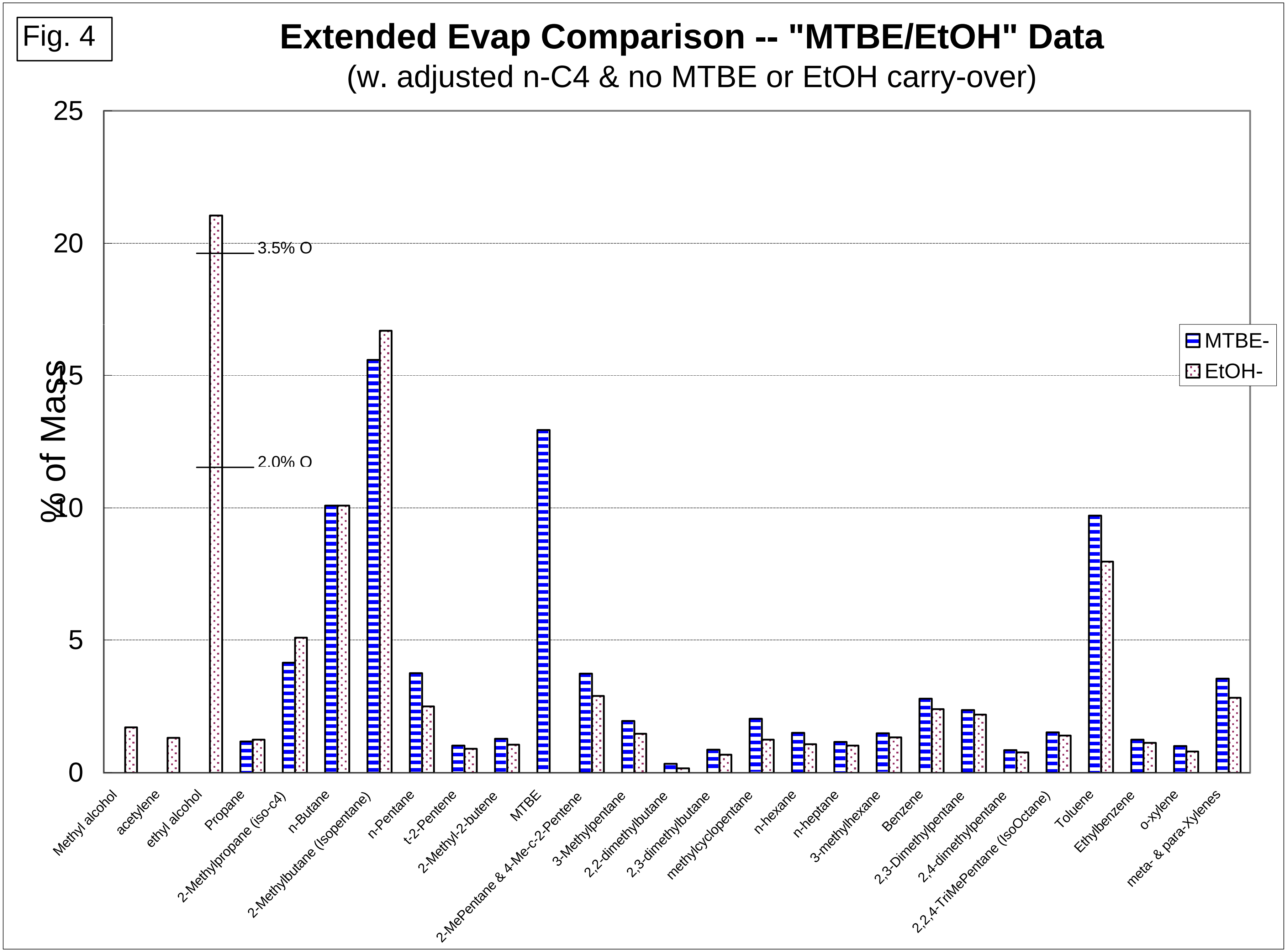


Fig. 4
Extended Evap Comparison -- "MTBE/EtOH" Data
(w. adjusted n-C4 & no MTBE or EtOH carry-over)
% of Mass
25
20
15
10
5
0
3.5% O
2.0% O
MTBE-
EtOH-
Methyl alcohol
acetylene
ethyl alcohol
Propane
2-Methylpropane (iso-c4)
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
t-2-Pentene
2-Methyl-2-butene
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
2,2-dimethylbutane
2,3-dimethylbutane
methylcyclopentane
n-hexane
n-heptane
3-methylhexane
Benzene
2,3-Dimethylpentane
2,4-dimethylpentane
2,2,4-TriMePentane (IsoOctane)
Toluene
Ethylbenzene
o-xylene
meta- & para-Xylenes

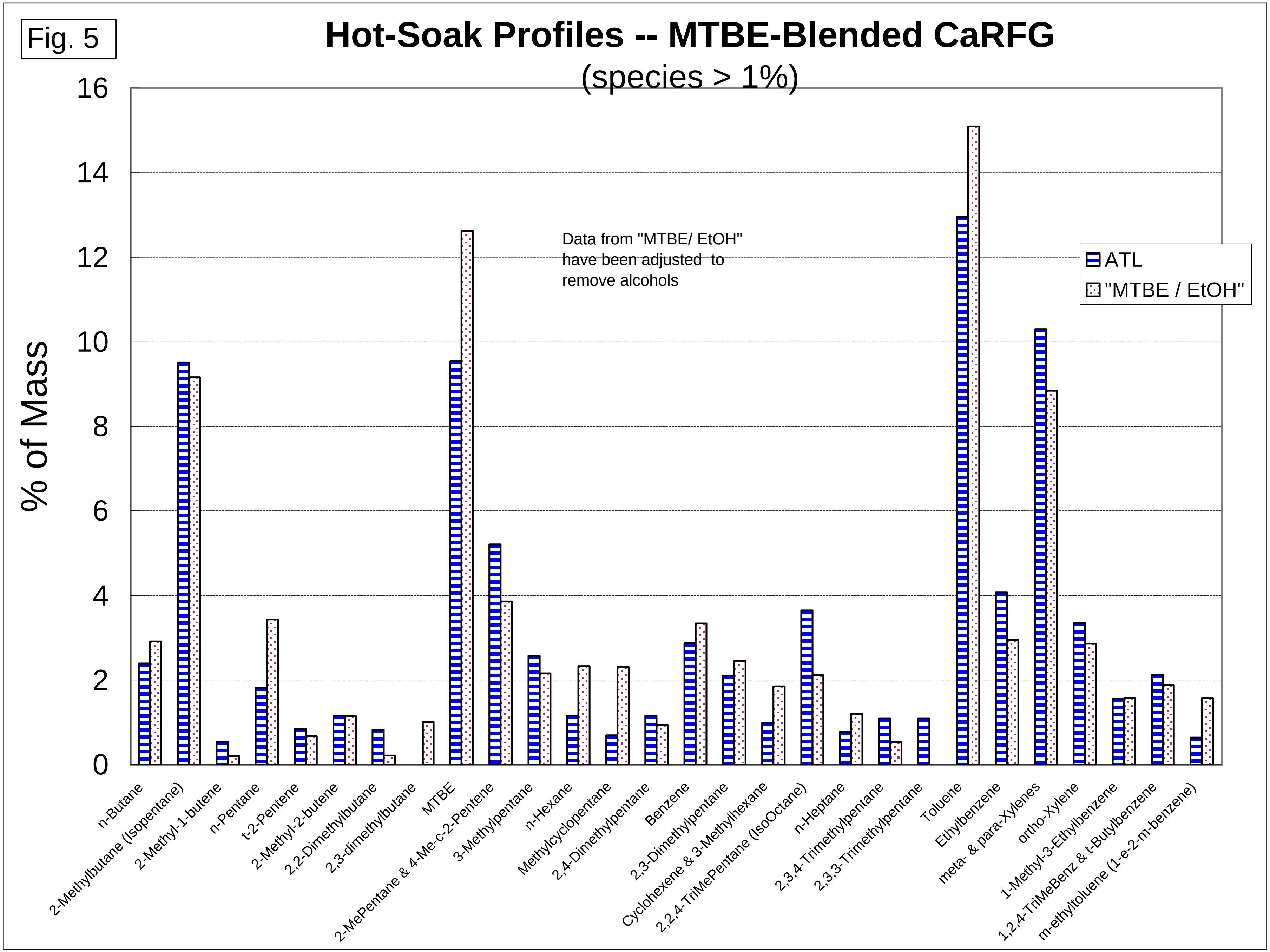


Fig. 5
Hot-Soak Profiles -- MTBE-Blended CaRFG
(species > 1%)
% of Mass
0
2
4
6
8
10
12
14
16
Data from "MTBE/ EtOH" have been adjusted to remove alcohols
ATL
"MTBE / EtOH"
n-Butane
2-Methylbutane (Isopentane)
2-Methyl-1-butene
n-Pentane
t-2-Pentene
2-Methyl-2-butene
2,2-Dimethylbutane
2,3-dimethylbutane
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
Cyclohexene & 3-Methylhexane
2,2,4-TriMePentane (IsoOctane)
n-Heptane
2,3,4-Trimethylpentane
2,3,3-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
m-ethyltoluene (1-e-2-m-benzene)

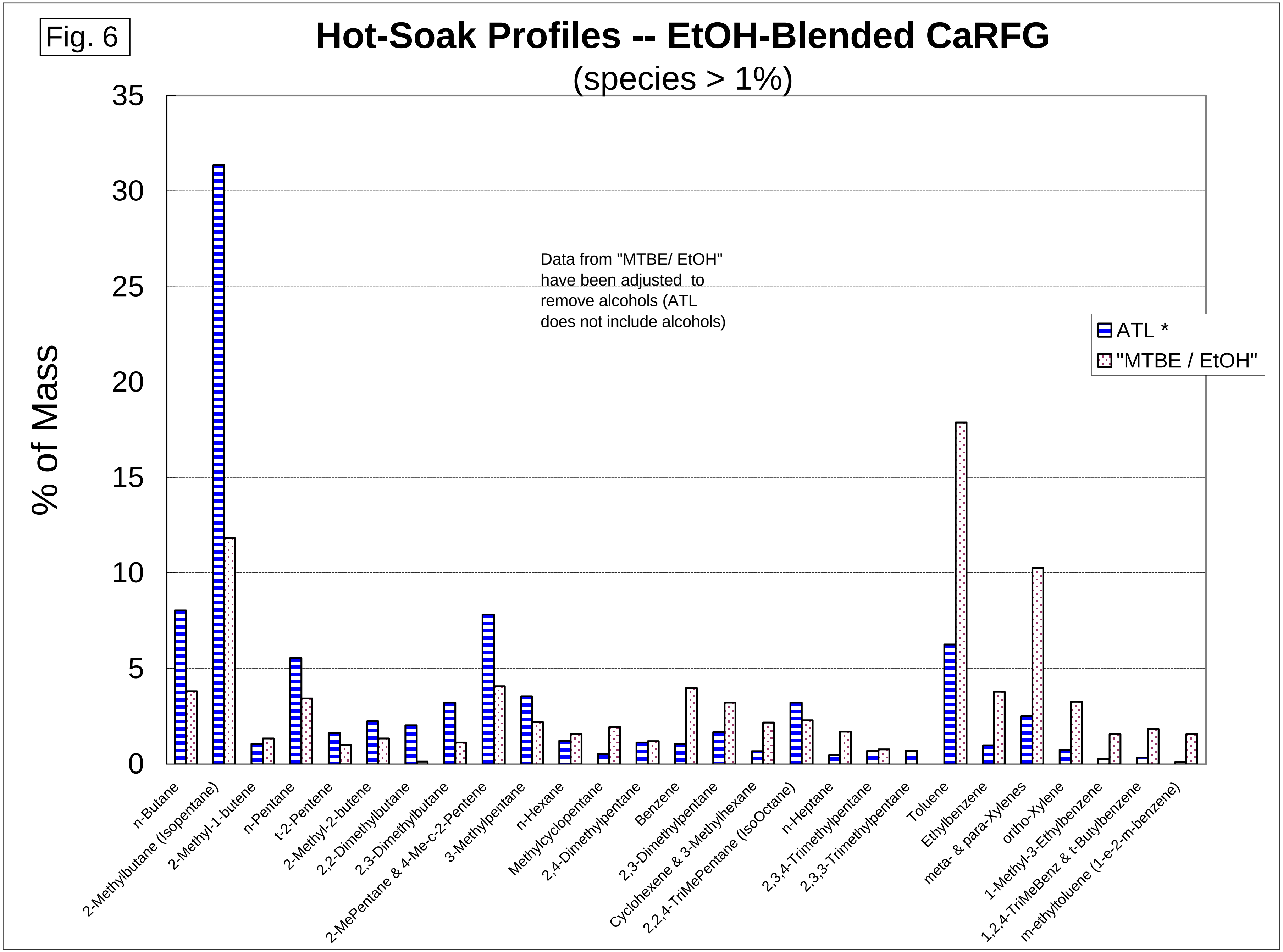


Fig. 6
Hot-Soak Profiles -- EtOH-Blended CaRFG
(species > 1%)
% of Mass
35
30
25
20
15
10
5
0
Data from "MTBE/ EtOH" have been adjusted to remove alcohols (ATL does not include alcohols)
ATL *
"MTBE / EtOH"
n-Butane
2-Methylbutane (Isopentane)
2-Methyl-1-butene
n-Pentane
t-2-Pentene
2-Methyl-2-butene
2,2-Dimethylbutane
2,3-Dimethylbutane
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
Cyclohexene & 3-Methylhexane
2,2,4-TriMePentane (IsoOctane)
n-Heptane
2,3,4-Trimethylpentane
2,3,3-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
m-ethyltoluene (1-e-2-m-benzene)

Fig. 7

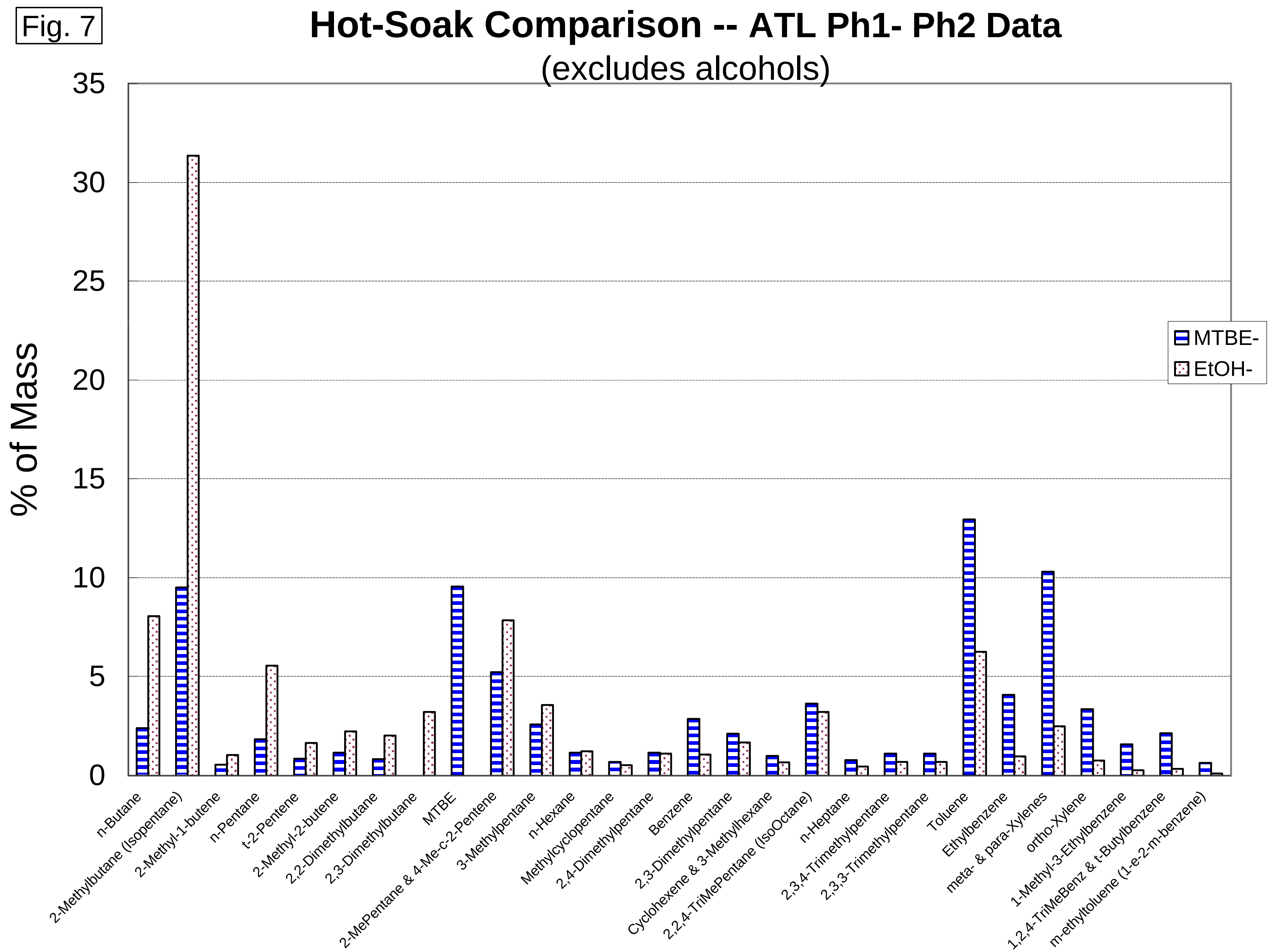
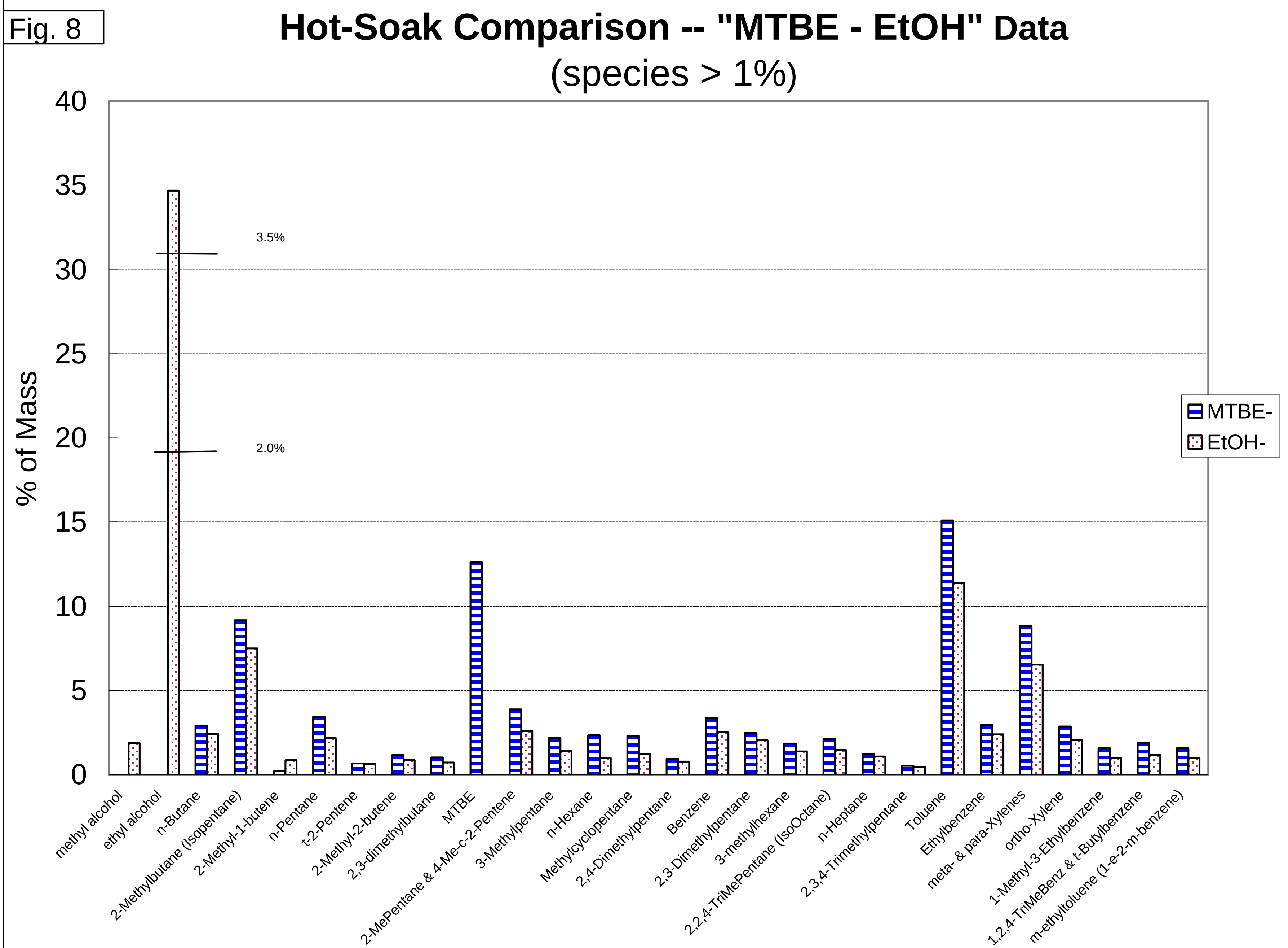

Hot-Soak Comparison -- ATL Ph1- Ph2 Data
(excludes alcohols)
% of Mass
35
30
25
20
15
10
5
0
MTBE-
EtOH-
n-Butane
2-Methylbutane (Isopentane)
2-Methyl-1-butene
n-Pentane
t-2-Pentene
2-Methyl-2-butene
2,2-Dimethylbutane
2,3-Dimethylbutane
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
Cyclohexene & 3-Methylhexane
2,2,4-TriMePentane (IsoOctane)
n-Heptane
2,3,4-Trimethylpentane
2,3,3-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
m-ethyltoluene (1-e-2-m-benzene)

Fig. 8



Hot-Soak Comparison -- "MTBE - EtOH" Data
(species > 1%)
% of Mass
0
5
10
15
20
25
30
35
40
3.5%
2.0%
MTBE-
EtOH-
methyl alcohol
ethyl alcohol
n-Butane
2-Methylbutane (Isopentane)
2-Methyl-1-butene
n-Pentane
t-2-Pentene
2-Methyl-2-butene
2,3-dimethylbutane
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
3-methylhexane
2,2,4-TriMePentane (IsoOctane)
n-Heptane
2,3,4-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
m-ethyltoluene (1-e-2-m-benzene)

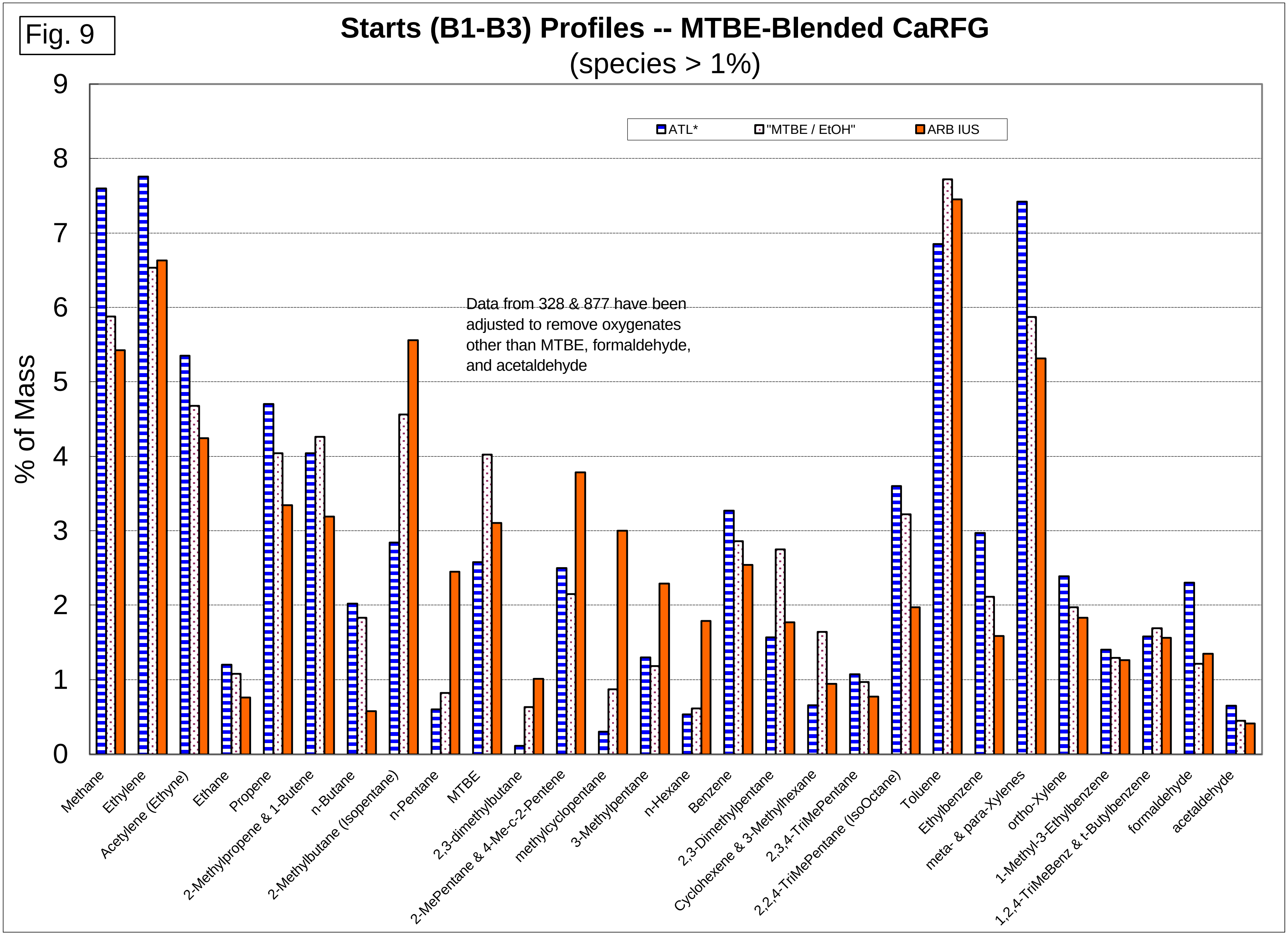


Fig. 9
Starts (B1-B3) Profiles -- MTBE-Blended CaRFG
(species > 1%)
ATL*
"MTBE / EtOH"
ARB IUS
Data from 328 & 877 have been adjusted to remove oxygenates other than MTBE, formaldehyde, and acetaldehyde
% of Mass
0
1
2
3
4
5
6
7
8
9
Methane
Ethylene
Acetylene (Ethyne)
Ethane
Propene
2-Methylpropene & 1-Butene
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
MTBE
2,3-dimethylbutane
2-MePentane & 4-Me-c-2-Pentene
methylcyclopentane
3-Methylpentane
n-Hexane
Benzene
2,3-Dimethylpentane
Cyclohexene & 3-Methylhexane
2,3,4-TriMePentane
2,2,4-TriMePentane (IsoOctane)
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
formaldehyde
acetaldehyde

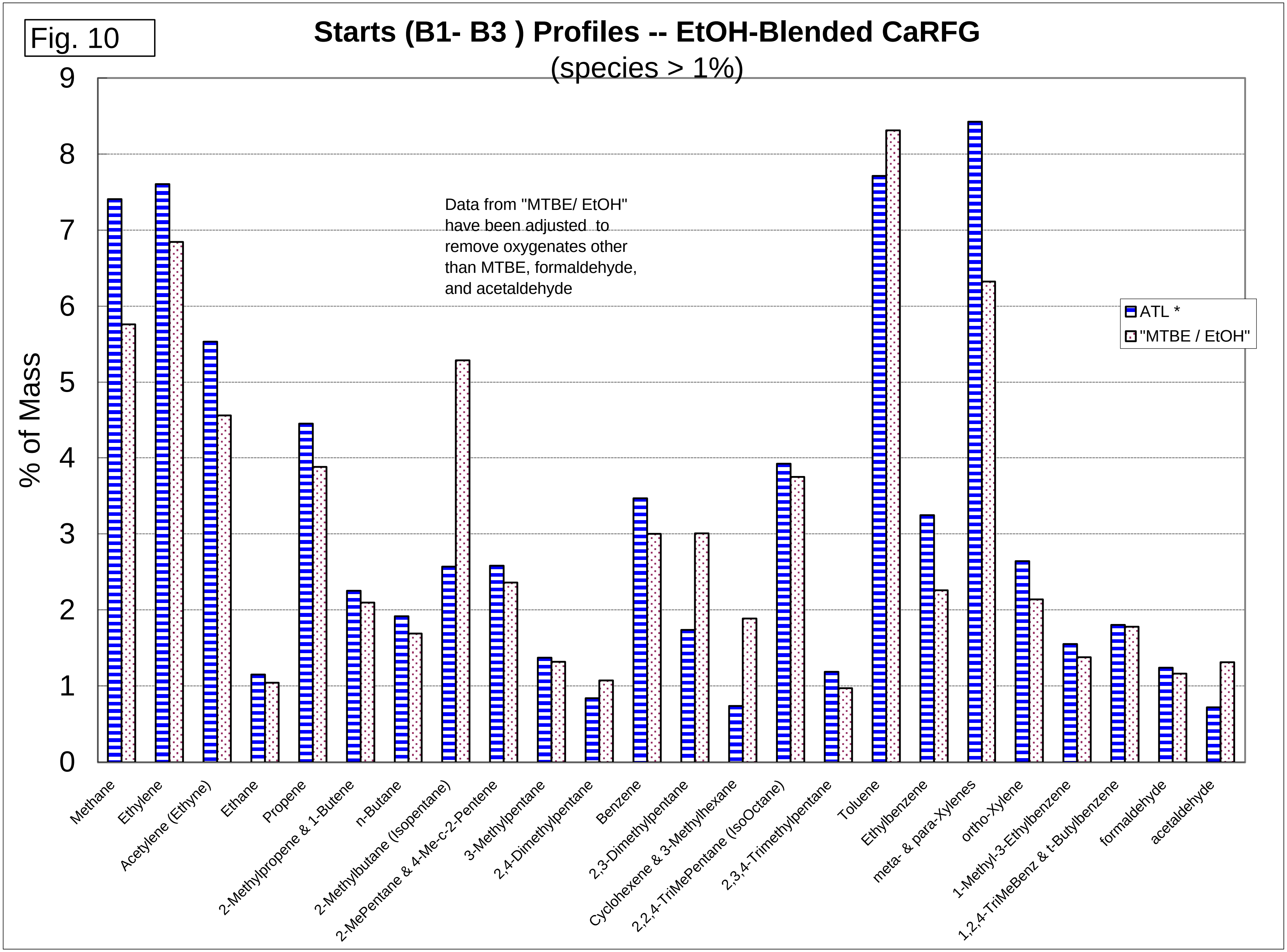


Fig. 10
Starts (B1- B3) Profiles -- EtOH-Blended CaRFG
(species > 1%)
% of Mass
0
1
2
3
4
5
6
7
8
9
Data from "MTBE/ EtOH" have been adjusted to remove oxygenates other than MTBE, formaldehyde, and acetaldehyde
ATL *
"MTBE / EtOH"
Methane
Ethylene
Acetylene (Ethyne)
Ethane
Propene
2-Methylpropene & 1-Butene
n-Butane
2-Methylbutane (Isopentane)
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
Cyclohexene & 3-Methylhexane
2,2,4-TriMePentane (IsoOctane)
2,3,4-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
formaldehyde
acetaldehyde

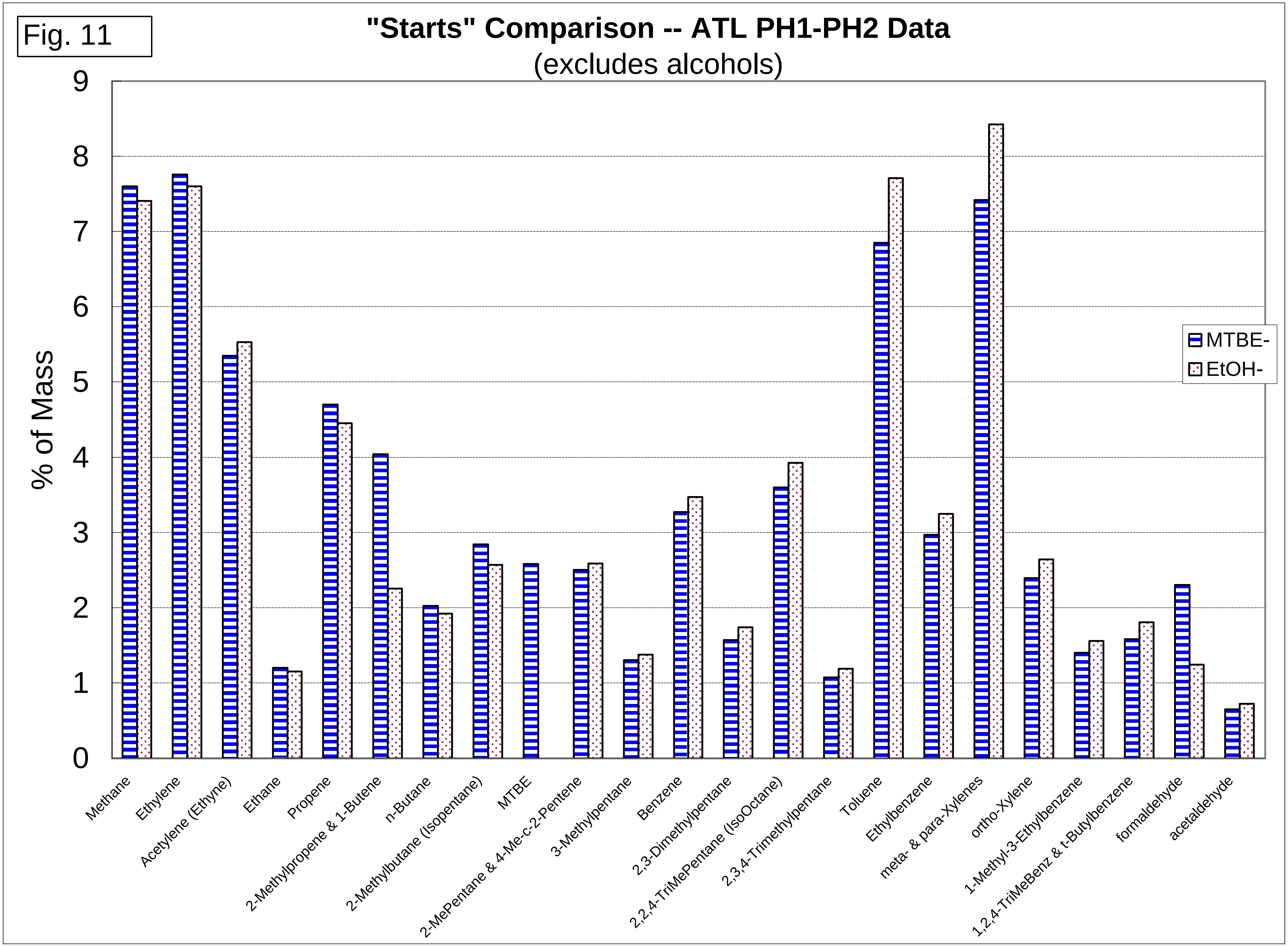


Fig. 11
"Starts" Comparison -- ATL PH1-PH2 Data
(excludes alcohols)
% of Mass
0
1
2
3
4
5
6
7
8
9
MTBE-
EtOH-
Methane
Ethylene
Acetylene (Ethyne)
Ethane
Propene
2-Methylpropene & 1-Butene
n-Butane
2-Methylbutane (Isopentane)
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
Benzene
2,3-Dimethylpentane
2,2,4-TriMePentane (IsoOctane)
2,3,4-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
formaldehyde
acetaldehyde

Fig. 12

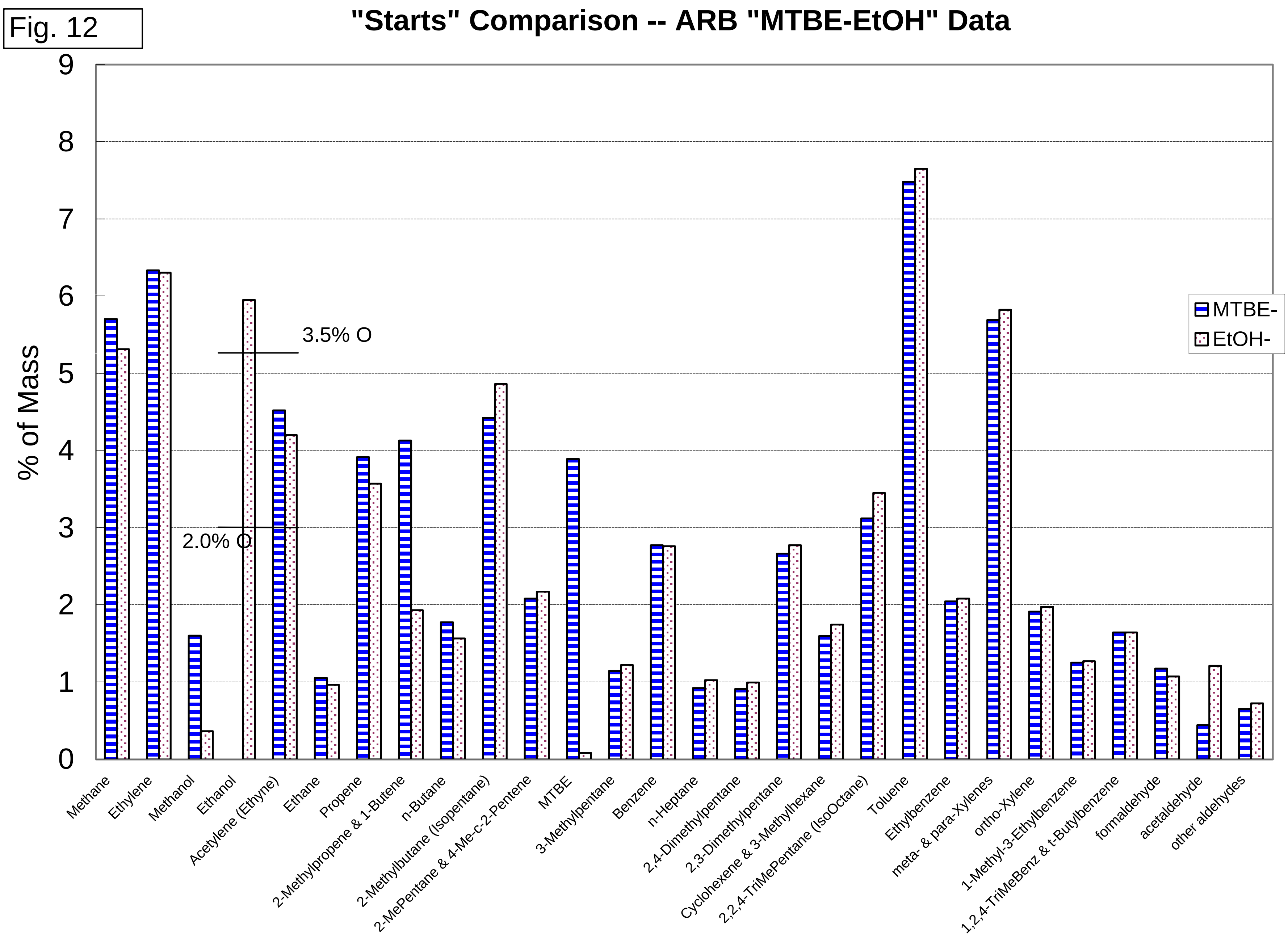

"Starts" Comparison -- ARB "MTBE-EtOH" Data
% of Mass
0
1
2
3
4
5
6
7
8
9
3.5% O
2.0% O
MTBE-
EtOH-
Methane
Ethylene
Methanol
Ethanol
Acetylene (Ethyne)
Ethane
Propene
2-Methylpropene & 1-Butene
n-Butane
2-Methylbutane (Isopentane)
2-MePentane & 4-Me-c-2-Pentene
MTBE
3-Methylpentane
Benzene
n-Heptane
2,4-Dimethylpentane
2,3-Dimethylpentane
Cyclohexene & 3-Methylhexane
2,2,4-TriMePentane (IsoOctane)
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
formaldehyde
acetaldehyde
other aldehydes

Fig. 13

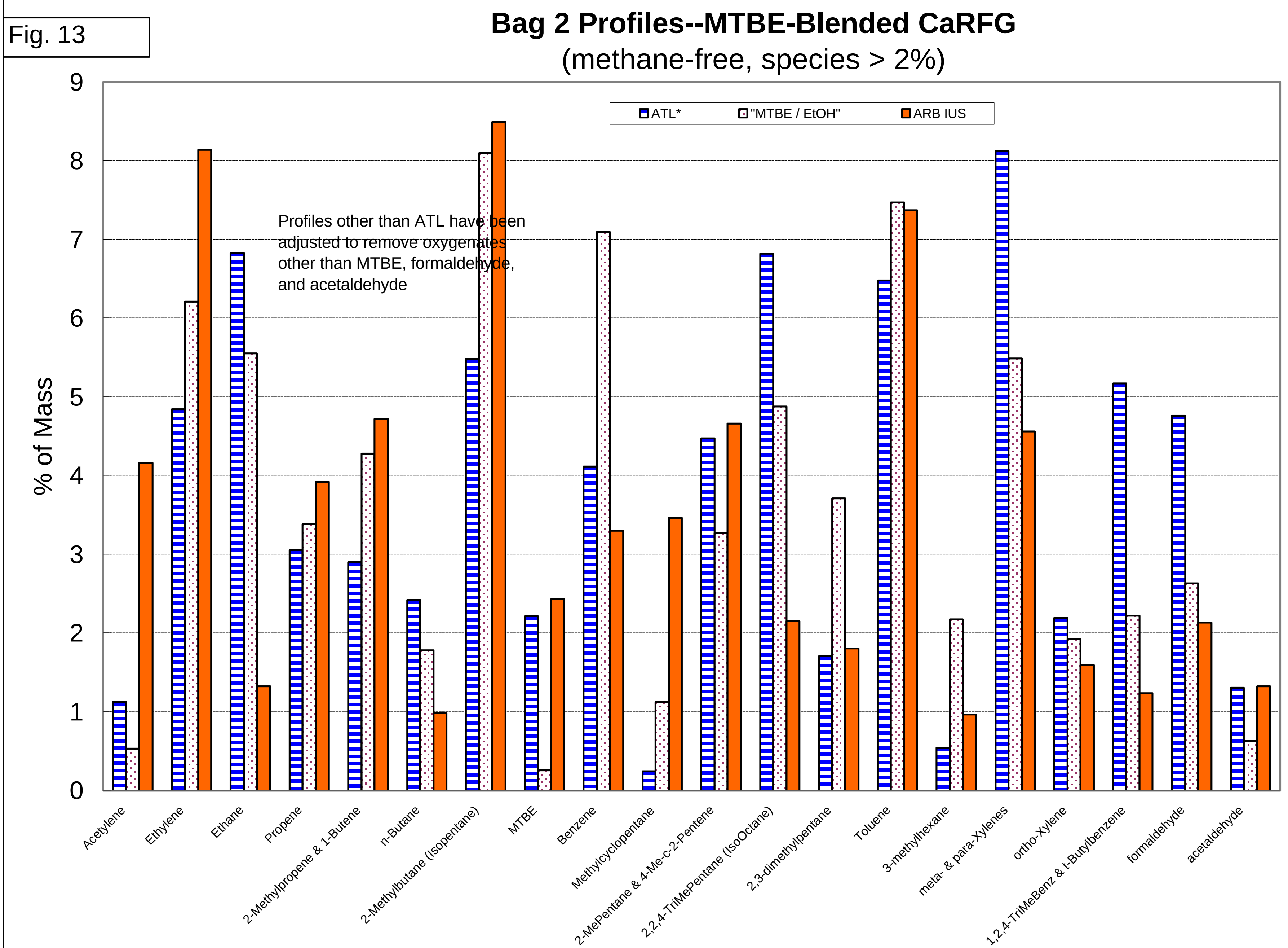
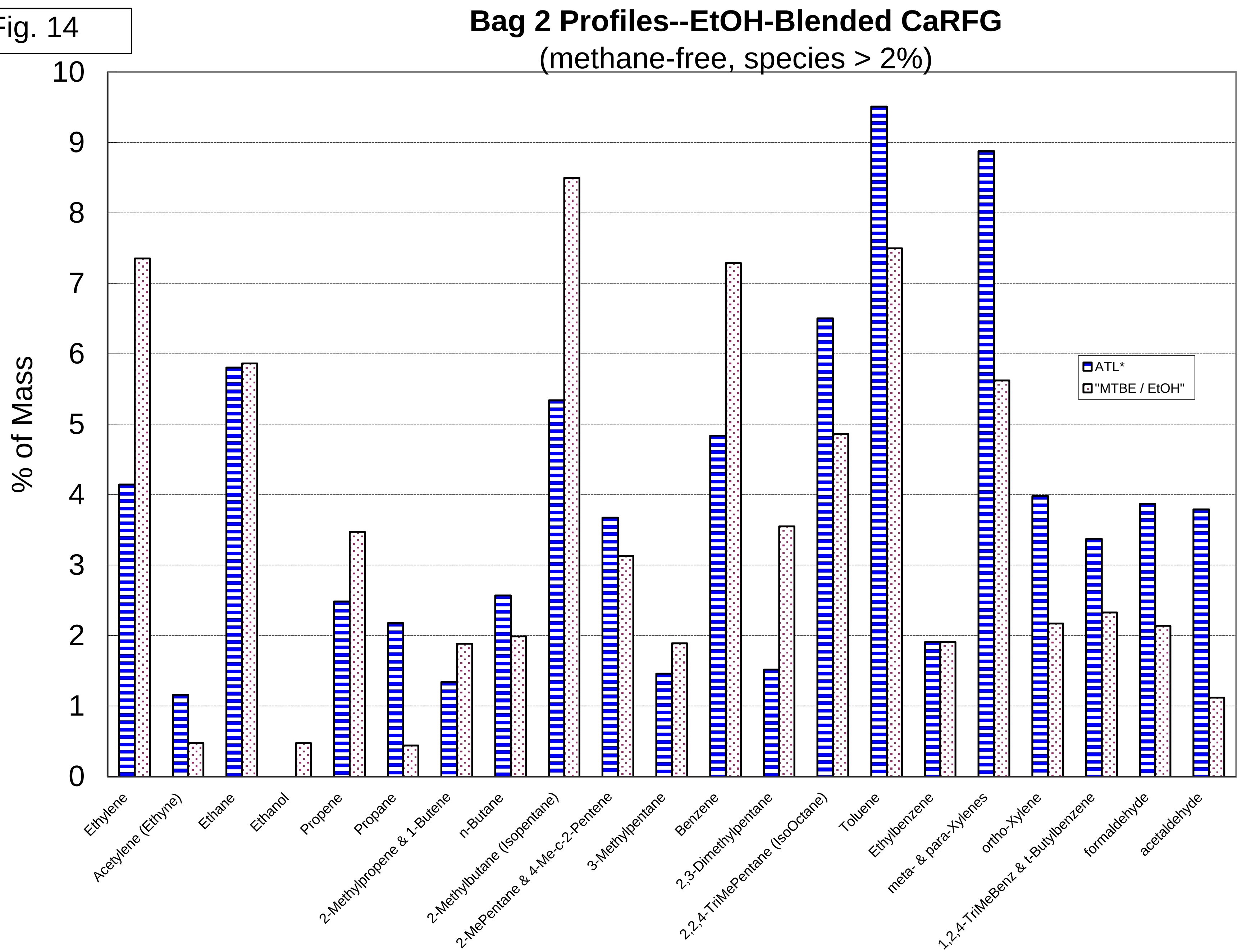
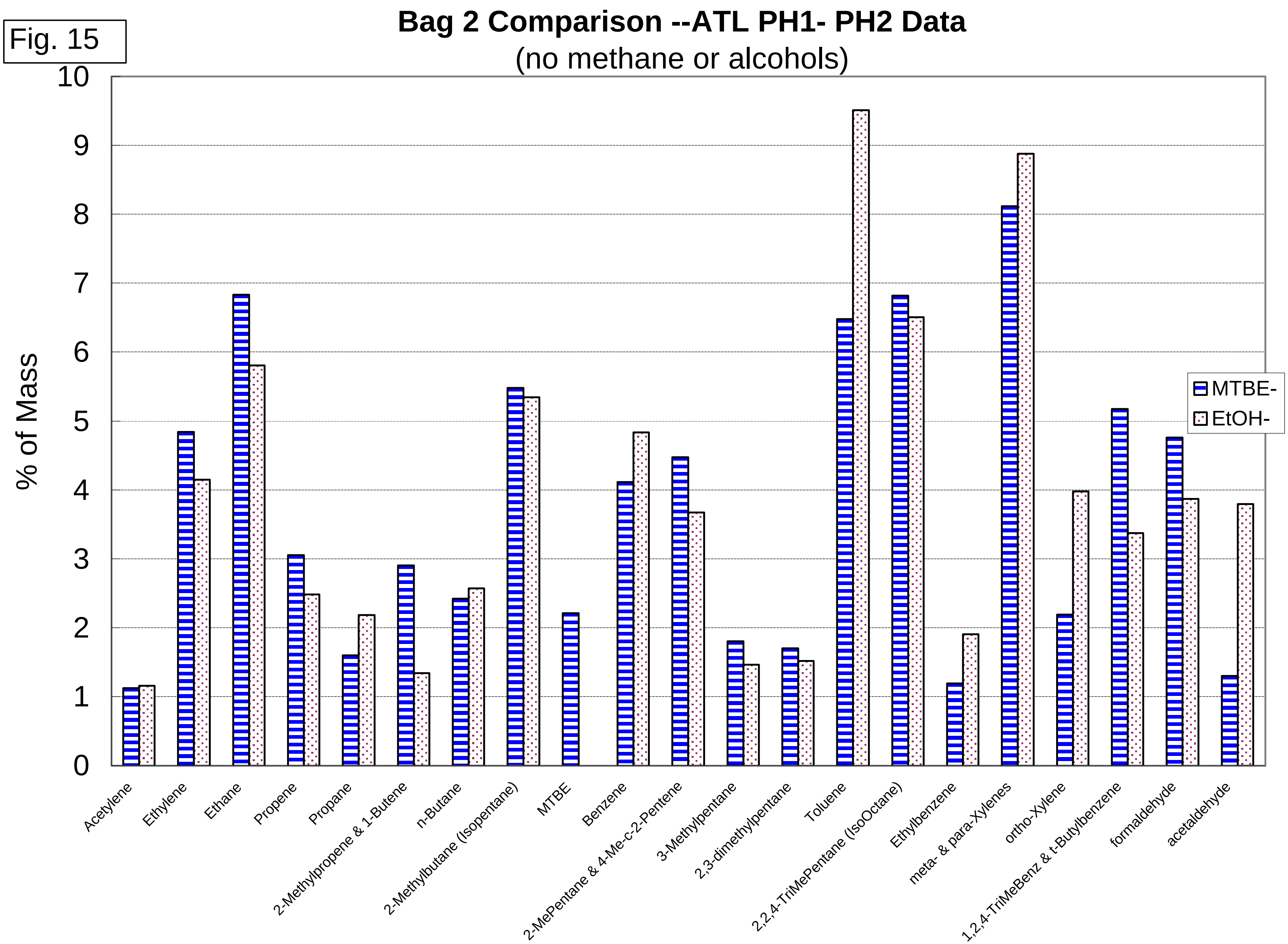

Bag 2 Profiles--MTBE-Blended CaRFG
(methane-free, species > 2%)
ATL*
"MTBE / EtOH"
ARB IUS
Profiles other than ATL have been adjusted to remove oxygenates other than MTBE, formaldehyde, and acetaldehyde
% of Mass
0
1
2
3
4
5
6
7
8
9
Acetylene
Ethylene
Ethane
Propene
2-Methylpropene & 1-Butene
n-Butane
2-Methylbutane (Isopentane)
MTBE
Benzene
Methylcyclopentane
2-MePentane & 4-Me-c-2-Pentene
2,2,4-TriMePentane (IsoOctane)
2,3-dimethylpentane
Toluene
3-methylhexane
meta- & para-Xylenes
ortho-Xylene
1,2,4-TriMeBenz & t-Butylbenzene
formaldehyde
acetaldehyde

Fig. 14



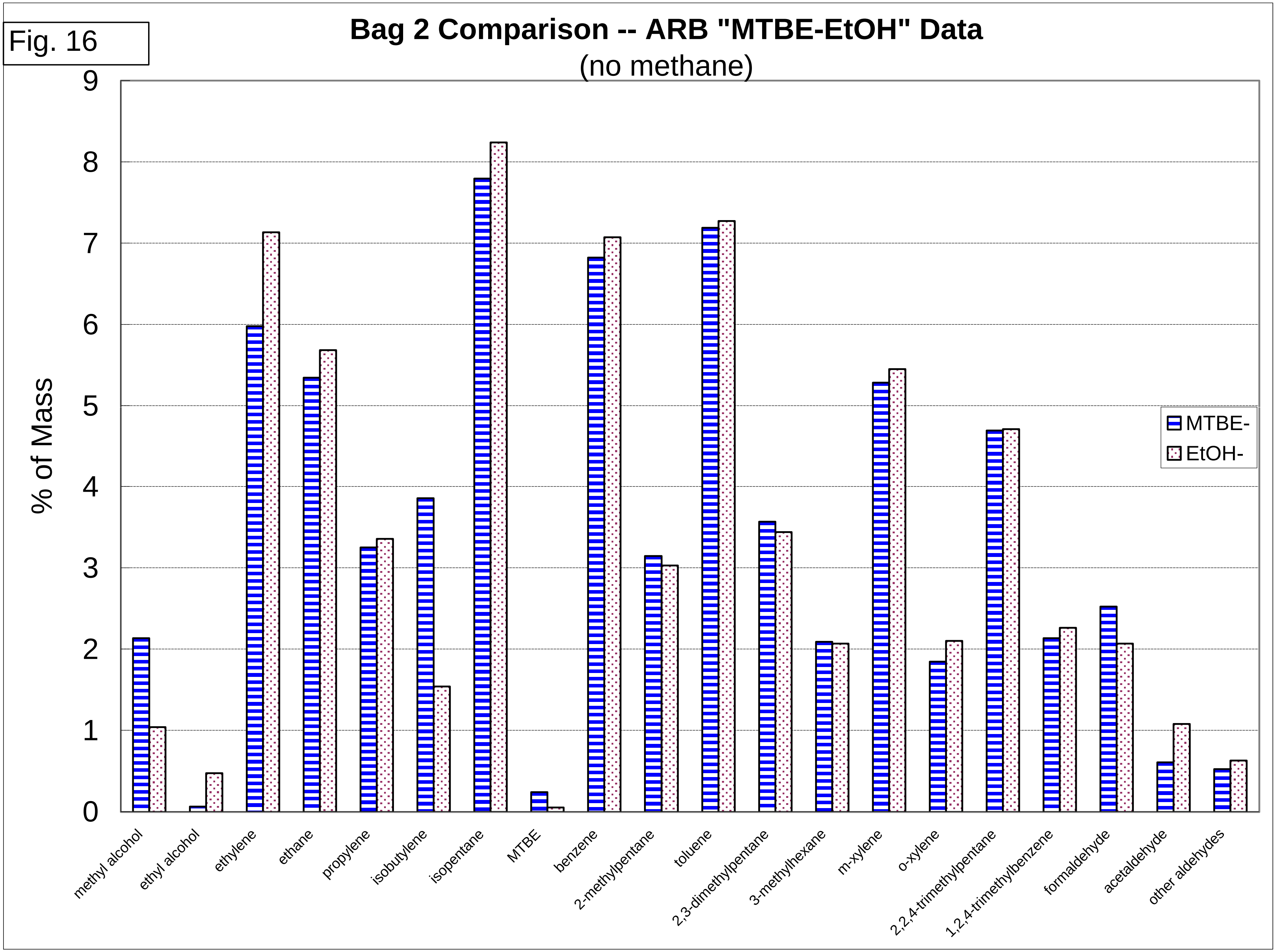
Bag 2 Profiles--EtOH-Blended CaRFG
(methane-free, species > 2%)
% of Mass
0
1
2
3
4
5
6
7
8
9
10
ATL*
"MTBE / EtOH"
Ethylene
Acetylene (Ethyne)
Ethane
Ethanol
Propene
Propane
2-Methylpropene & 1-Butene
n-Butane
2-Methylbutane (Isopentane)
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
Benzene
2,3-Dimethylpentane
2,2,4-TriMePentane (IsoOctane)
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1,2,4-TriMeBenz & t-Butylbenzene
formaldehyde
acetaldehyde

Fig. 15



Bag 2 Comparison --ATL PH1- PH2 Data
(no methane or alcohols)
% of Mass
0
1
2
3
4
5
6
7
8
9
10
MTBE-
EtOH-
Acetylene
Ethylene
Ethane
Propene
Propane
2-Methylpropene & 1-Butene
n-Butane
2-Methylbutane (Isopentane)
MTBE
Benzene
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
2,3-dimethylpentane
Toluene
2,2,4-TriMePentane (IsoOctane)
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1,2,4-TriMeBenz & t-Butylbenzene
formaldehyde
acetaldehyde

Fig. 16



Bag 2 Comparison -- ARB "MTBE-EtOH" Data
(no methane)
% of Mass
0
1
2
3
4
5
6
7
8
9
MTBE-
EtOH-
methyl alcohol
ethyl alcohol
ethylene
ethane
propylene
isobutylene
isopentane
MTBE
benzene
2-methylpentane
toluene
2,3-dimethylpentane
3-methylhexane
m-xylene
o-xylene
2,2,4-trimethylpentane
1,2,4-trimethylbenzene
formaldehyde
acetaldehyde
other aldehydes

Fig. 17

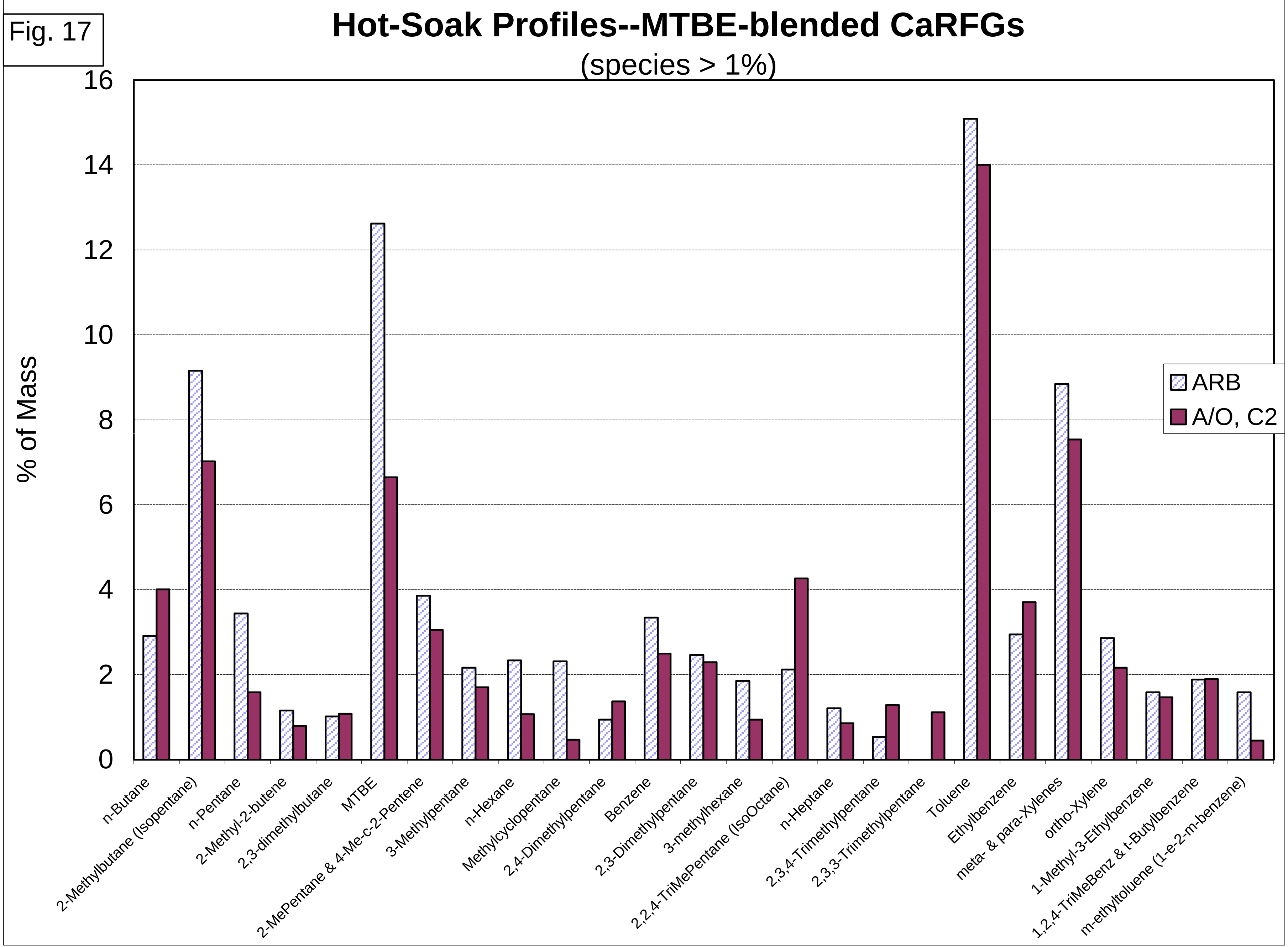

Hot-Soak Profiles--MTBE-blended CaRFGs
(species > 1%)
% of Mass
0
2
4
6
8
10
12
14
16
ARB
A/O, C2
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
2-Methyl-2-butene
2,3-dimethylbutane
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
3-methylhexane
2,2,4-TriMePentane (IsoOctane)
n-Heptane
2,3,4-Trimethylpentane
2,3,3-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene
m-ethyltoluene (1-e-2-m-benzene)

Fig. 18

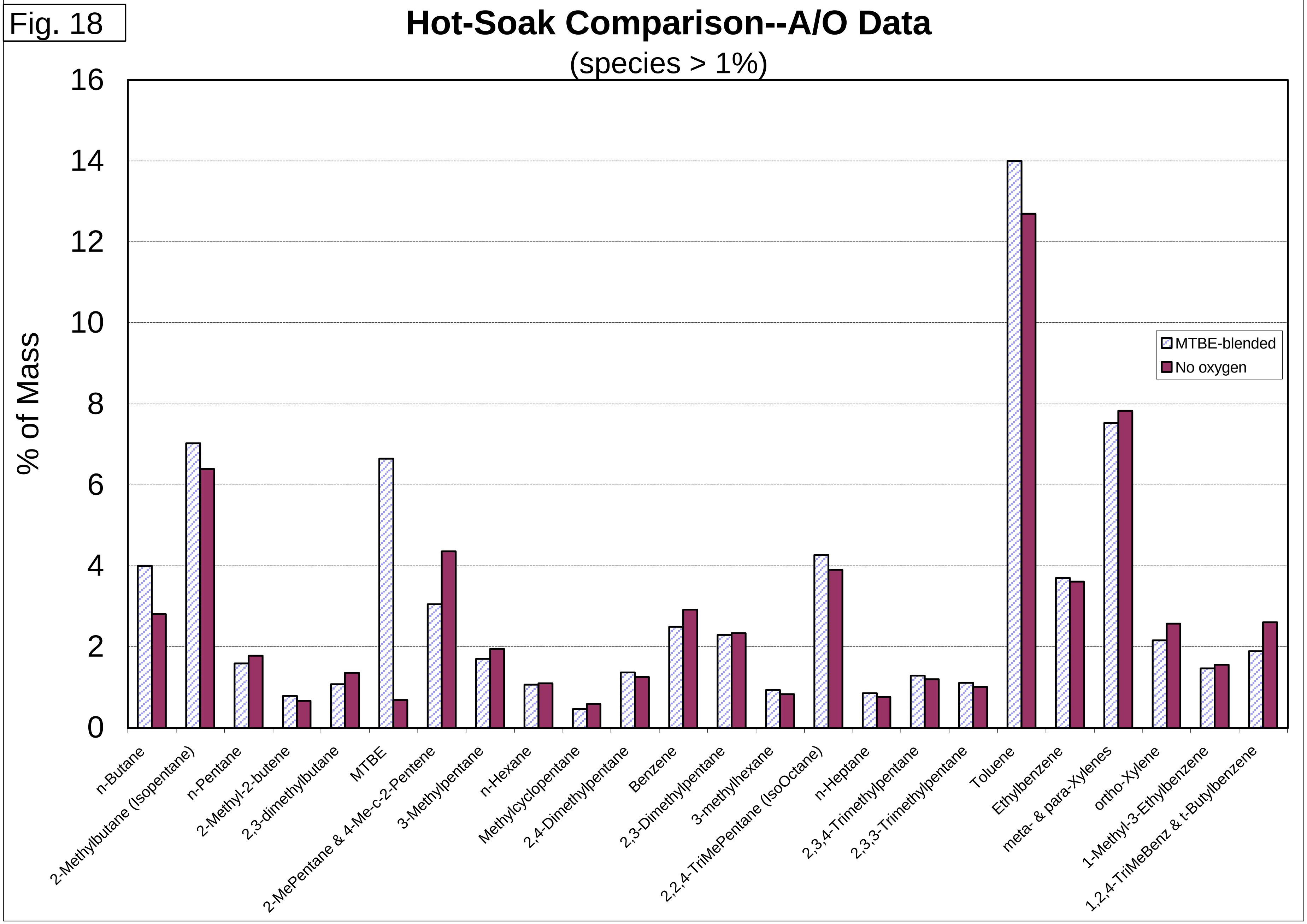
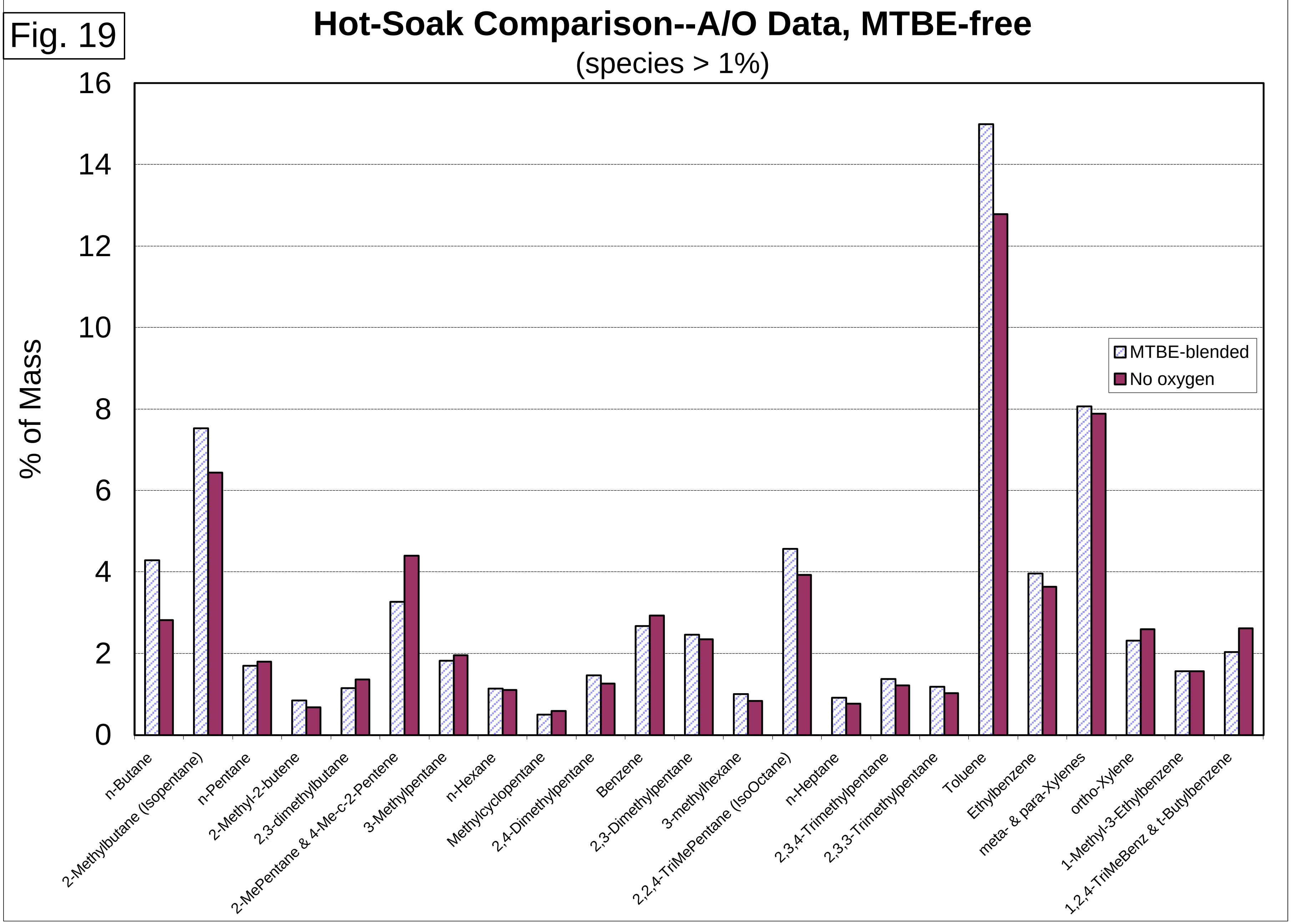

Hot-Soak Comparison--A/O Data
(species > 1%)
% of Mass
0
2
4
6
8
10
12
14
16
MTBE-blended
No oxygen
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
2-Methyl-2-butene
2,3-dimethylbutane
MTBE
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
3-methylhexane
2,2,4-TriMePentane (IsoOctane)
n-Heptane
2,3,4-Trimethylpentane
2,3,3-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene

Fig. 19



Hot-Soak Comparison--A/O Data, MTBE-free
(species > 1%)
% of Mass
0
2
4
6
8
10
12
14
16
MTBE-blended
No oxygen
n-Butane
2-Methylbutane (Isopentane)
n-Pentane
2-Methyl-2-butene
2,3-dimethylbutane
2-MePentane & 4-Me-c-2-Pentene
3-Methylpentane
n-Hexane
Methylcyclopentane
2,4-Dimethylpentane
Benzene
2,3-Dimethylpentane
3-methylhexane
2,2,4-TriMePentane (IsoOctane)
n-Heptane
2,3,4-Trimethylpentane
2,3,3-Trimethylpentane
Toluene
Ethylbenzene
meta- & para-Xylenes
ortho-Xylene
1-Methyl-3-Ethylbenzene
1,2,4-TriMeBenz & t-Butylbenzene

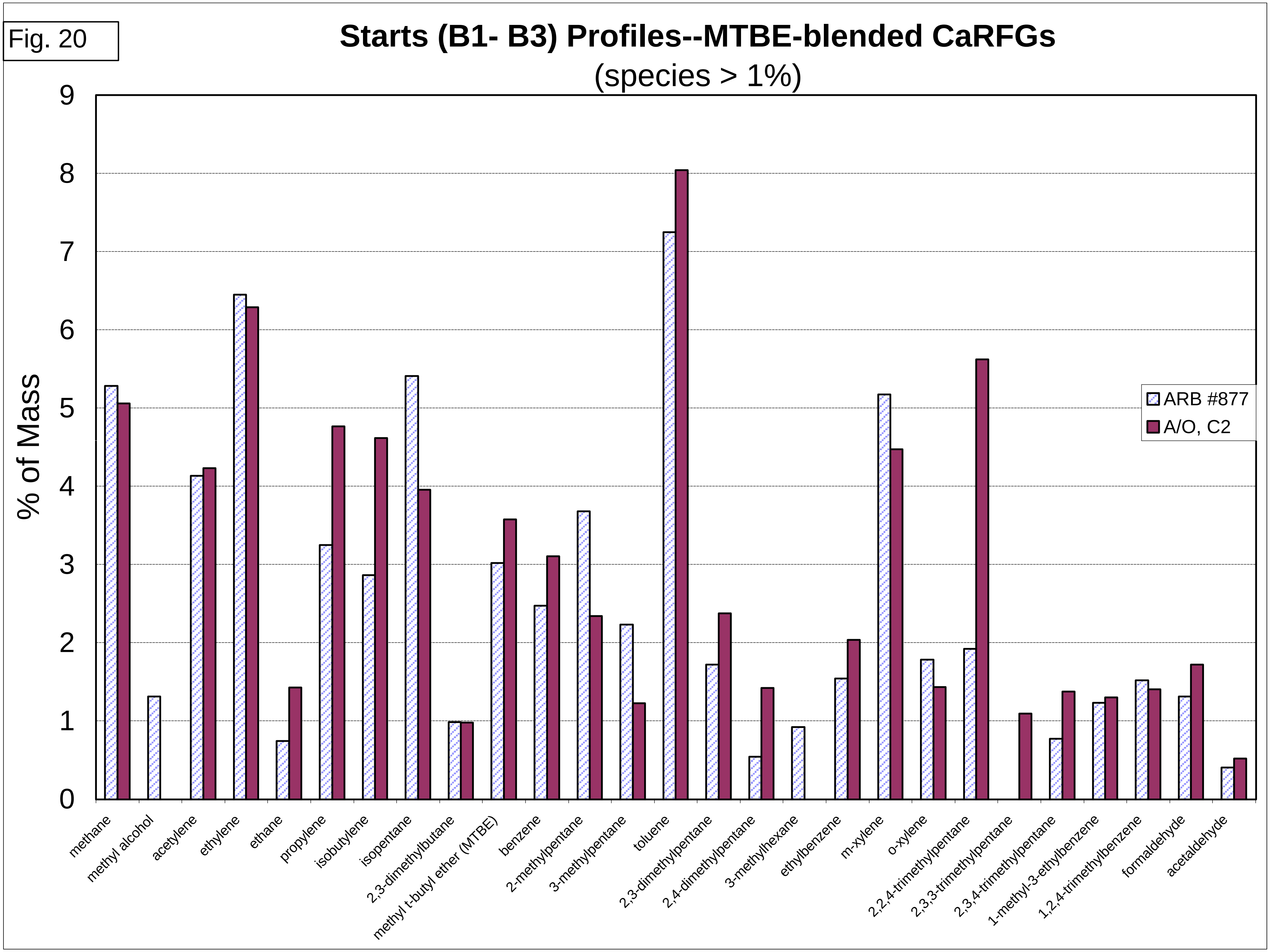


Fig. 20
Starts (B1- B3) Profiles--MTBE-blended CaRFGs
(species > 1%)
% of Mass
0
1
2
3
4
5
6
7
8
9
ARB #877
A/O, C2
methane
methyl alcohol
acetylene
ethylene
ethane
propylene
isobutylene
isopentane
2,3-dimethylbutane
methyl t-butyl ether (MTBE)
benzene
2-methylpentane
3-methylpentane
toluene
2,3-dimethylpentane
2,4-dimethylpentane
3-methylhexane
ethylbenzene
m-xylene
o-xylene
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
1-methyl-3-ethylbenzene
1,2,4-trimethylbenzene
formaldehyde
acetaldehyde

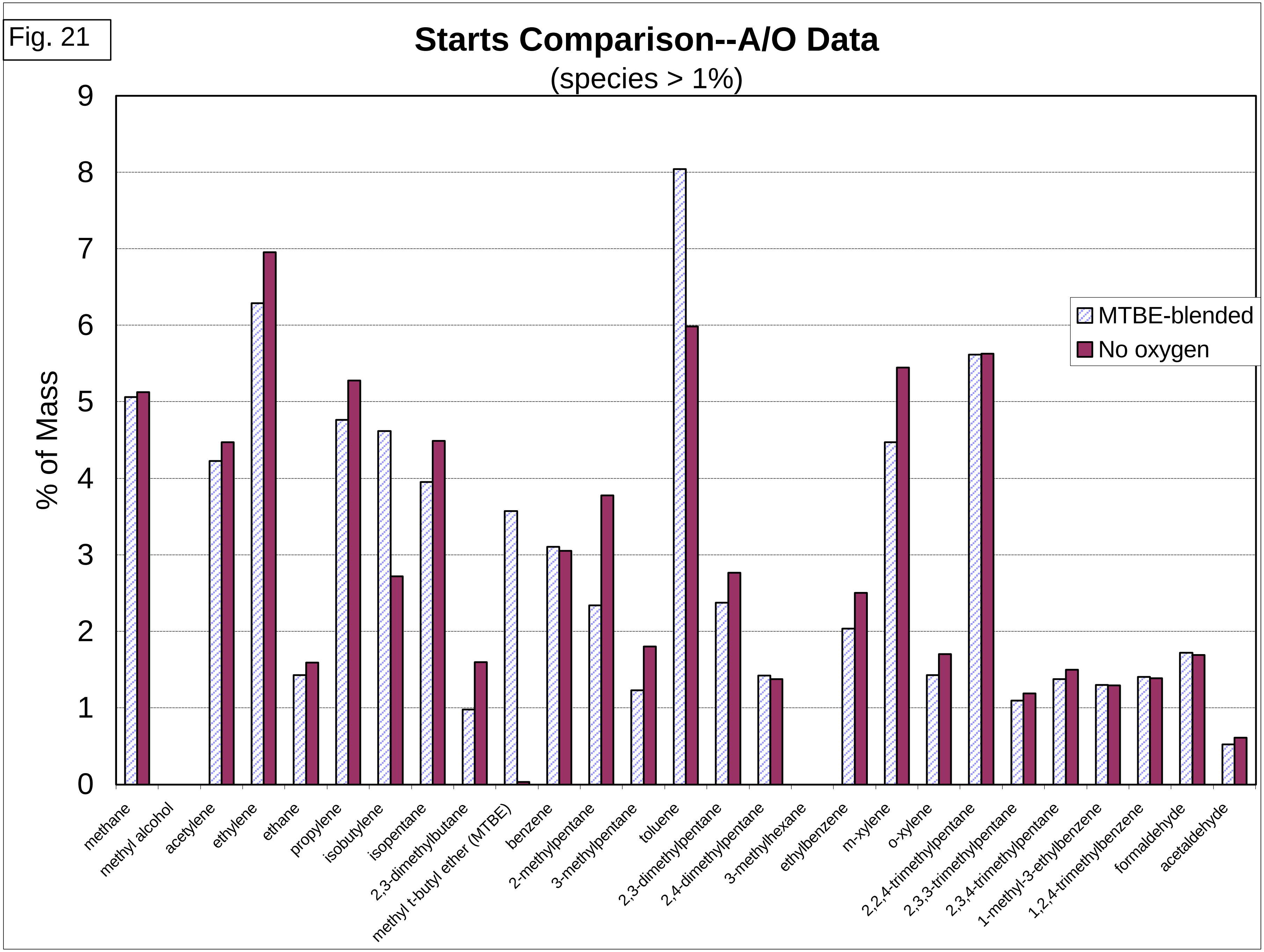
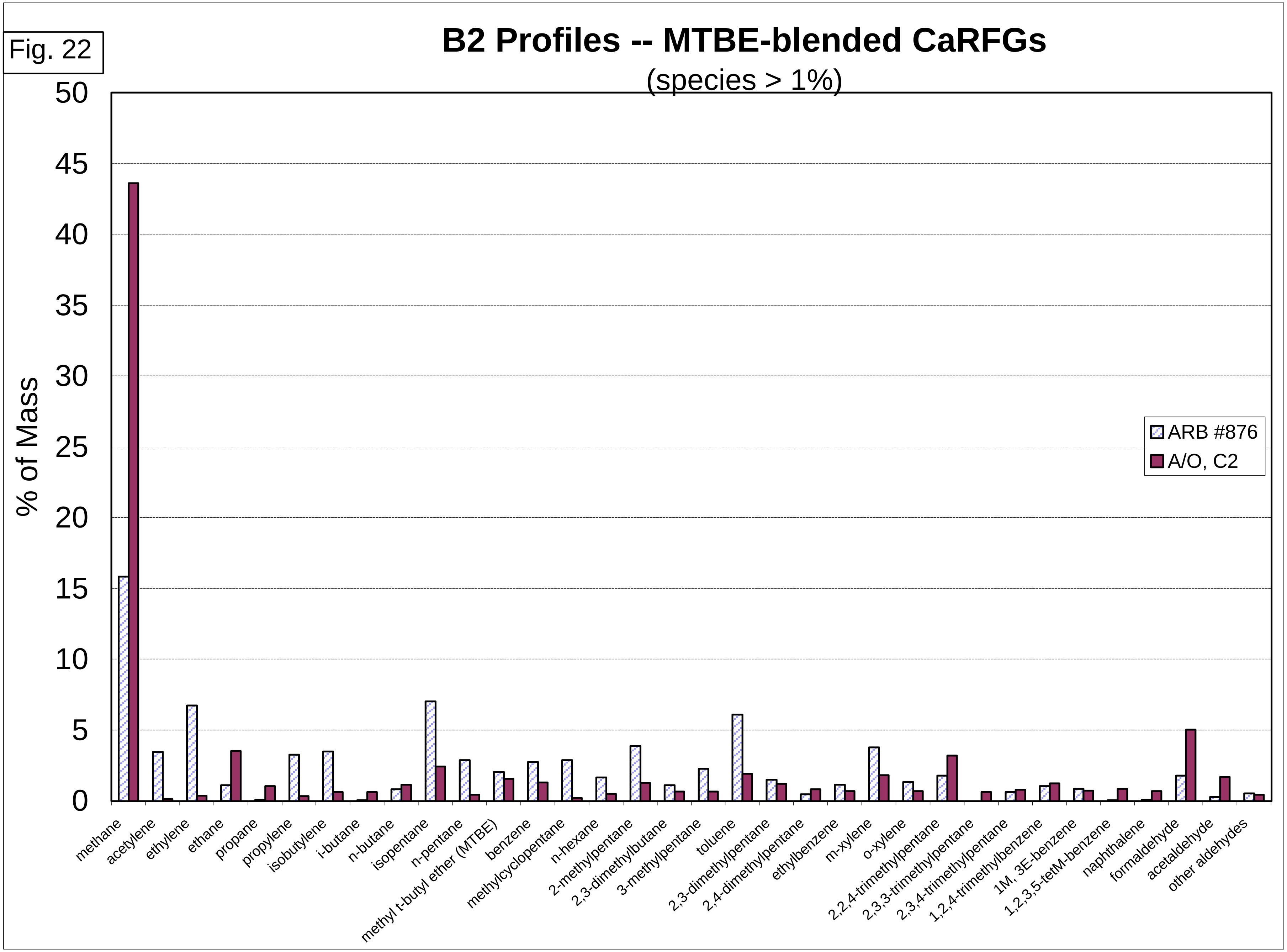


Fig. 21
Starts Comparison--A/O Data
(species > 1%)
% of Mass
0
1
2
3
4
5
6
7
8
9
MTBE-blended
No oxygen
methane
methyl alcohol
acetylene
ethylene
ethane
propylene
isobutylene
isopentane
2,3-dimethylbutane
methyl t-butyl ether (MTBE)
benzene
2-methylpentane
3-methylpentane
toluene
2,3-dimethylpentane
2,4-dimethylpentane
3-methylhexane
ethylbenzene
m-xylene
o-xylene
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
1-methyl-3-ethylbenzene
1,2,4-trimethylbenzene
formaldehyde
acetaldehyde

Fig. 22


B2 Profiles -- MTBE-blended CaRFGs
(species > 1%)
% of Mass
50
45
40
35
30
25
20
15
10
5
0
ARB #876
A/O, C2
methane
acetylene
ethylene
ethane
propane
propylene
isobutylene
i-butane
n-butane
isopentane
n-pentane
methyl t-butyl ether (MTBE)
benzene
methylcyclopentane
n-hexane
2-methylpentane
2,3-dimethylbutane
3-methylpentane
toluene
2,3-dimethylpentane
2,4-dimethylpentane
ethylbenzene
m-xylene
o-xylene
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
1,2,4-trimethylbenzene
1M, 3E-benzene
1,2,3,5-tetM-benzene
naphthalene
formaldehyde
acetaldehyde
other aldehydes

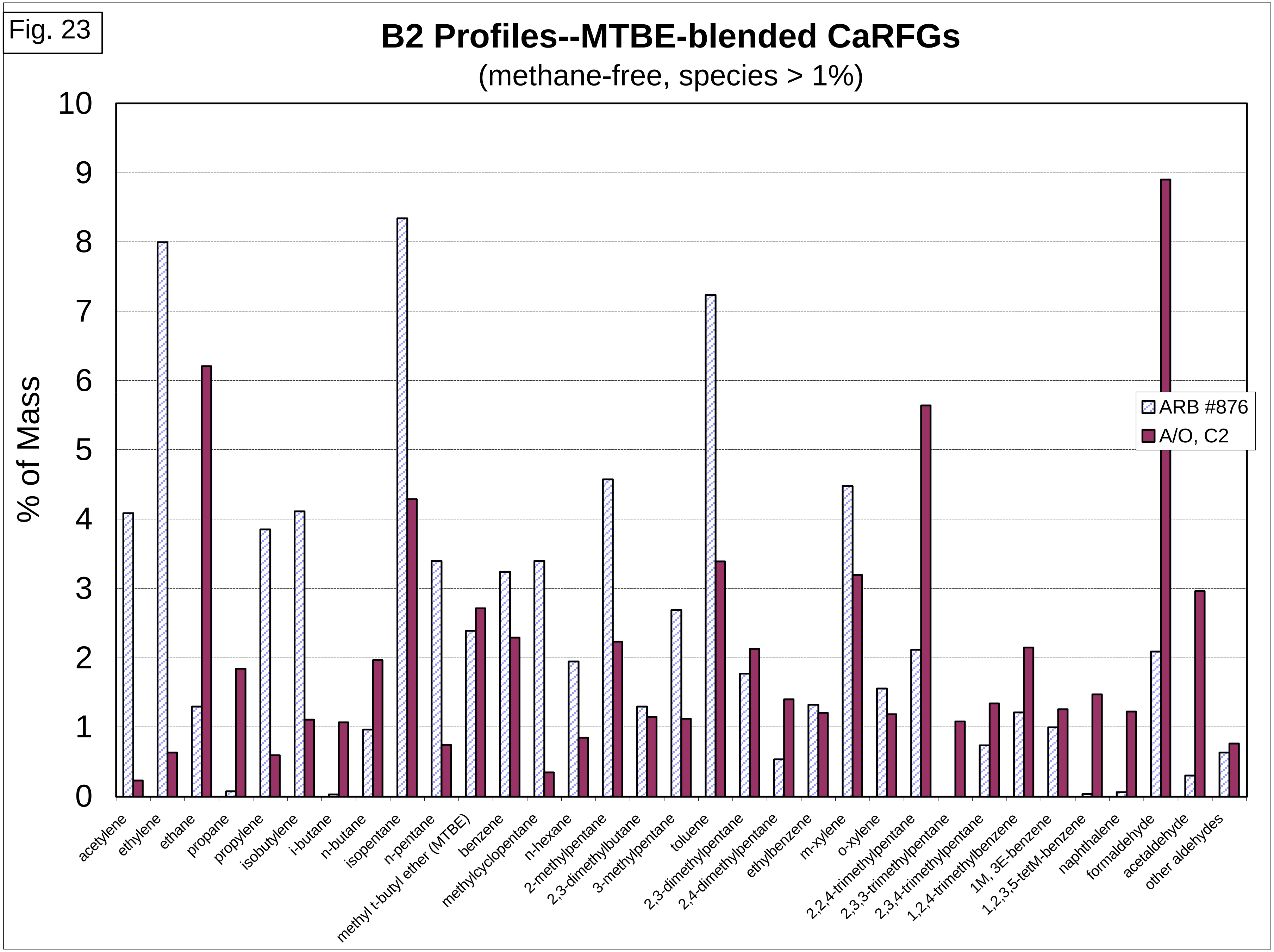


Fig. 23
B2 Profiles--MTBE-blended CaRFGs
(methane-free, species > 1%)
% of Mass
0
1
2
3
4
5
6
7
8
9
10
ARB #876
A/O, C2
acetylene
ethylene
ethane
propane
propylene
isobutylene
i-butane
n-butane
isopentane
n-pentane
methyl t-butyl ether (MTBE)
benzene
methylcyclopentane
n-hexane
2-methylpentane
2,3-dimethylbutane
3-methylpentane
toluene
2,3-dimethylpentane
2,4-dimethylpentane
ethylbenzene
m-xylene
o-xylene
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
1,2,4-trimethylbenzene
1M, 3E-benzene
1,2,3,5-tetM-benzene
naphthalene
formaldehyde
acetaldehyde
other aldehydes

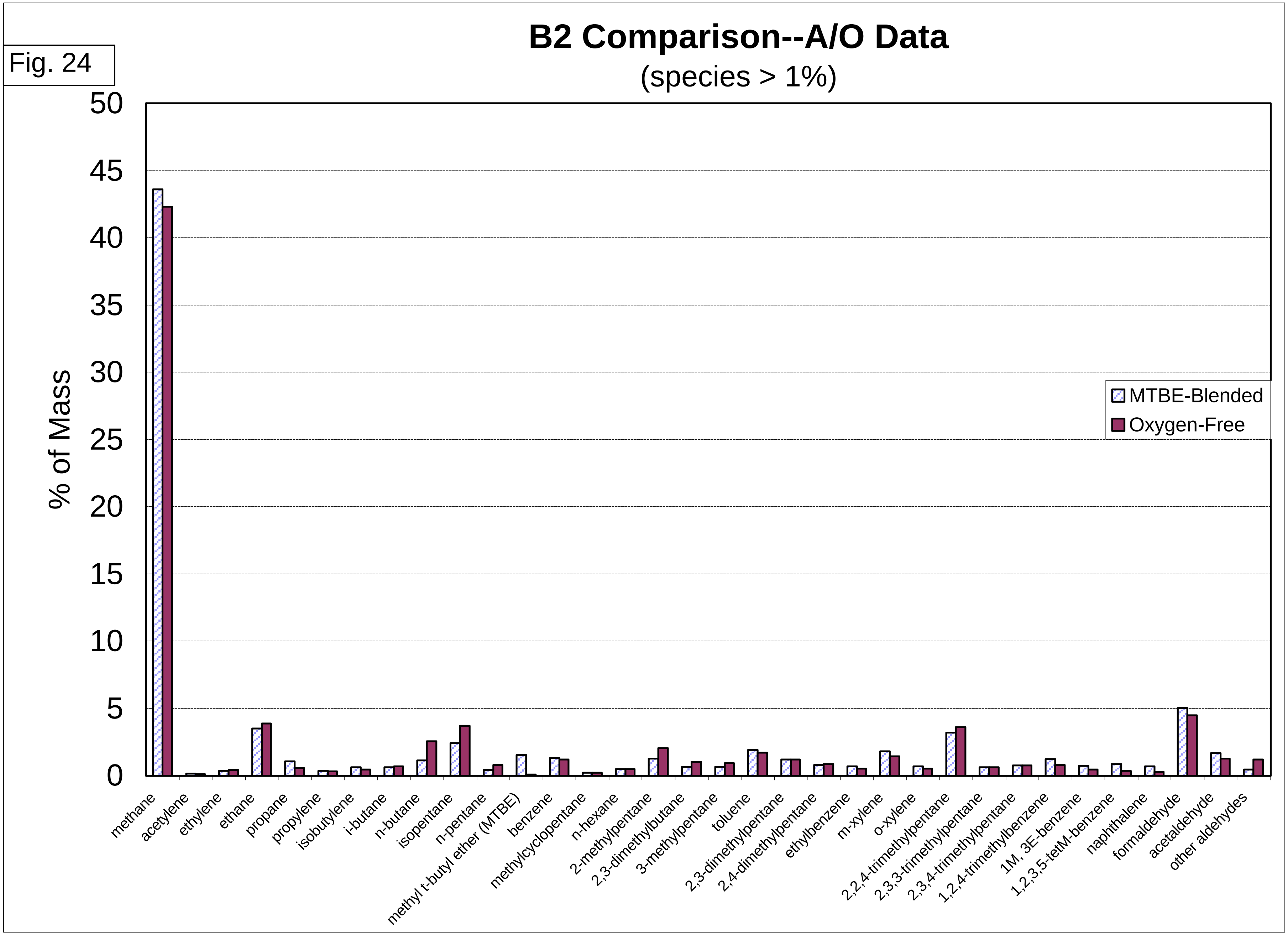
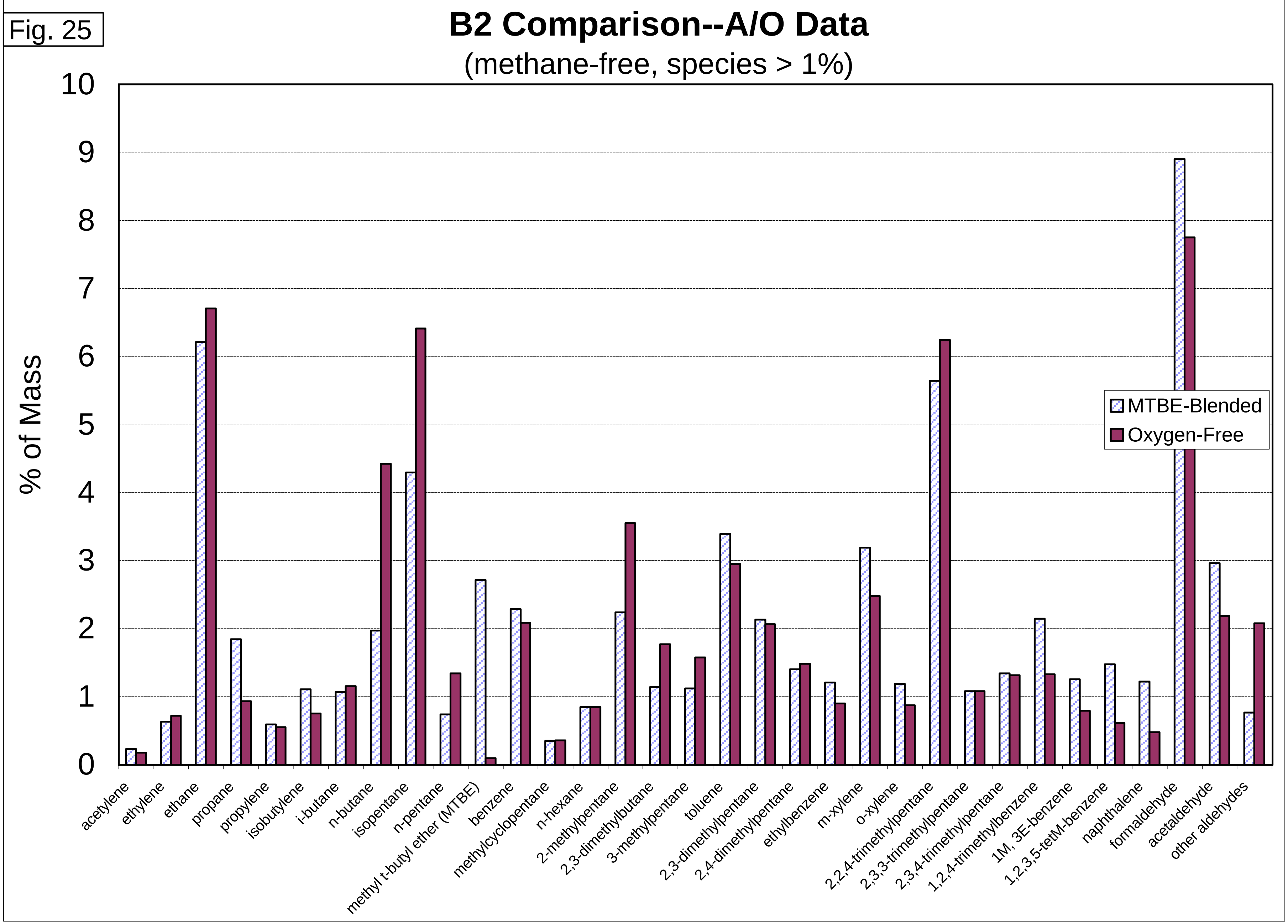


Fig. 24
B2 Comparison--A/O Data
(species > 1%)
% of Mass
0
5
10
15
20
25
30
35
40
45
50
MTBE-Blended
Oxygen-Free
methane
acetylene
ethylene
ethane
propane
propylene
isobutylene
i-butane
n-butane
isopentane
n-pentane
methyl t-butyl ether (MTBE)
benzene
methylcyclopentane
n-hexane
2-methylpentane
2,3-dimethylbutane
3-methylpentane
toluene
2,3-dimethylpentane
2,4-dimethylpentane
ethylbenzene
m-xylene
o-xylene
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
1,2,4-trimethylbenzene
1M, 3E-benzene
1,2,3,5-tetM-benzene
naphthalene
formaldehyde
acetaldehyde
other aldehydes

Fig. 25



B2 Comparison--A/O Data
(methane-free, species > 1%)
% of Mass
0
1
2
3
4
5
6
7
8
9
10
MTBE-Blended
Oxygen-Free
acetylene
ethylene
ethane
propane
propylene
isobutylene
i-butane
n-butane
isopentane
n-pentane
methyl t-butyl ether (MTBE)
benzene
methylcyclopentane
n-hexane
2-methylpentane
2,3-dimethylbutane
3-methylpentane
toluene
2,3-dimethylpentane
2,4-dimethylpentane
ethylbenzene
m-xylene
o-xylene
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
1,2,4-trimethylbenzene
1M, 3E-benzene
1,2,3,5-tetM-benzene
naphthalene
formaldehyde
acetaldehyde
other aldehydes